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Report Number WCDC-6465

• EFFECT OF PHASE CHANGE IN SOLID-SOLID REACTIONS (U)

Annual Report
by

Joseph H. McLain
Donald V. Lewis

January 31, 1966

U. S. Army Edgewood Arsenal
CHEMICAL RESEARCH & DEVELOPMENT LABORATORIES
Edgewood Arsenal, Maryland 21010

Grant: DA-AMC-18-035-77(A)

Department of Chemistry
WASHINGTON COLLEGE
Chestertown, Maryland

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Task: 1C014501B71A02

Department of Chemistry
WASHINGTON COLLEGE
Chester, Maryland

FOREWORD

The work described in this report was authorized under Task 1C014501B71A02, Life Sciences Basic Research in Support of Materiel, Chemical (U). This work was started in October 1964 and completed in October 1965. Additional experimental data are recorded in notebooks number W. C. I, II, and III.

Acknowledgments

The authors of the report wish to acknowledge the help and advice obtained from Mr. B. Zeffert and Mr. H. A. Brown, Jr. during the course of this work.

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DIGEST

Purpose: To investigate the reaction mechanism for the system $KClO_3 - S - NaHCO_3$ with emphasis on the detection of phase changes and their effect on the reaction.

Methods of Investigation: Differential thermal analysis, conductimetric thermal analysis, and burning rate studies have been used primarily for these investigations. A limited amount of measuring the effect of catalysts (positive and negative) to the burning rate of the fuel mix is included.

This investigation utilizes pure substances and binary mixtures of S and $KClO_3$. Measurements on thermal stability of modified crystalline forms of these components by the above methods are included.

Summary of Results:

1. DTA measurements show that profound changes can be brought about by treatment of the basic components.
2. Conductimetric methods correlated with DTA results have been partially successful.
3. An extremely reactive form of $KClO_3$ has been prepared.
4. A postulated reaction mechanism has been advanced.

Conclusions:

1. Conductimetric studies should be pursued especially in reactions of relatively small exotherms.
2. This system does undergo a preignition reaction which is dependent upon the previous history of the components.
3. Further experimental work is necessary to confirm the postulated reaction mechanism.
4. Copper metal and its salts represent a safety hazard in mixes of sulfur and potassium chlorate.

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EFFECT OF PHASE CHANGES ON SOLID-SOLID REACTIONS

I. Historical

There are two "fuel mixes" that have been used by the Chemical Corps for dissemination of agents in aerosol form such as dyes for signalling smokes and chloracetophenone or other lachrymators.

The oldest and most widely used of these is the fuel mix used in the M18 Colored Smoke grenades.

It was developed early in World War II by Dr. S. J. Magram and Lt. D. H. West (other names intimately associated at this time were W. P. Munro, J. C. Driskell and O. C. Tubbs), and is an essentially stoichiometric intimate mix of powdered sulfur and potassium chlorate and dye with varying amounts of sodium bicarbonate added as an alkalyzer and coolant. The amount of coolant needed is dependent upon the heat of sublimation of the agent and its sensitivity to pyrolytic decomposition.

(1)

A typical formulation is

Grenade, Smoke, Hand M18 (Red)

Dye	40 percent
NaHCO ₃	18 percent
KClO ₃	30.24 percent
S	11.76 percent

The KClO₃ - S ratio is stoichiometric for the reaction $2\text{KClO}_3 + 3\text{S} \rightarrow 3\text{SO}_2 + 2\text{KCl}$.

During and subsequent to World War II thousands of tons of this mix was made and loaded into munitions with excellent overall results. Yet there were some areas of significance for improvement. Of primary importance was that of safety. Fires on the rotex screens at Huntsville Arsenal during World War II although not commonplace happened all too frequently and caused loss of production as well as endangering personnel. Explosions or perhaps more exactly detonations have occurred when pressing and caused fatalities, the latest fire at Alton, Illinois in March 1965 which caused upwards of \$40,000.00 in property loss is an example.

Of subsidiary importance are some other factors, chief among which are ---

1. instability in storage
2. batch irreproducibility in production as evidenced by ---
 - (a) variation in burning time
 - (b) smoke quality (amount and color value)
 - (c) flamers
 - (d) fluffiness of mix which causes great difficulty and hazards in pressing operations
3. high cost of heat resistant dyes

Since World War II improvements of varying effectiveness have been made by the Chemical Corps and by the Navy. A typical Navy formulation⁽²⁾ is as follows:

KClO ₃	30 percent
Sucrose	20 percent
NaHCO ₃	10 percent
Dye	40 percent
Silocel	1 percent
Cabosil	1 percent

Aside from the elimination of any harmful properties attributable to the sulfur most of the foregoing disadvantages ascribed to the sulfur mix plus some others unique to sucrose apply to the Navy formulation.

As has been stated before, the results with the sulfur mix have been mainly successful and when it is remembered that this mix was developed under war time exigencies as to getting the optimum munition in the field within the shortest possible time and expense the overall success has been quite remarkable. Under this sort of pressure no time was permitted for a fundamental study as to complete effect of particle sizes, origin and analysis of the ingredients, pressure of loading and mixing variations to mention just a few.

Furthermore many of the techniques for measuring some of these effects were not even known or if known had not been applied to these sorts of systems. Consequently it was believed that just such a fundamental study should be undertaken and the physical chemistry laboratory at Washington College was awarded a research grant for this purpose.

For sake of completeness the work done by Heath⁽³⁾⁽⁴⁾ and co-workers at the Chemical Defense Experimental Station, Porton, England on the generation of insecticidal smokes from intimate mixtures should be discussed. In the first reference DDT (1:1 bis p-chlorophenyl 2:2:2 trichlorethane) and Gammexane (*r*-isomer of benzene hexachloride) were successfully sublimed from the following composition in 75% efficiency or better.

Sucrose	23%
KClO ₃	19%
DDT	58%

In actual use about 2% MgO was added in order to fix any hydrogen chloride that might be generated during tropical storage which could bring about premature ignition. It should be pointed out that efficiencies of 70 to 75% with DDT generation from an intimate mix are somewhat remarkable because even pure DDT begins to lose hydrogen chloride at 180° C and commercial DDT is more susceptible to decomposition.

The second reference reports even more remarkable efficiencies obtained with mixtures of urea-thiourea as fuel, potassium chlorate as

oxidizer and DDT as the agent. Efficiencies on mixtures containing 54.9% agent were as high as 90%.

Also a British patent⁽⁵⁹⁾ for an insecticide bomb reports the following typical composition.

lingane	60
KClO ₃	16.5
thiourea	11.5
Mineral filler	9
MgO	3

Colored smoke formulations have been made in Japan using sucrose and/or lactose as fuel⁶ and many of the same dyes used in this country.

The oxidizers have also been changed. A patent by T. L. Davis⁷ utilizes guanidine nitrate and nitro guanidine for a very "cool" burning composition and fireworks smokes are made using potassium nitrate, charcoal and realgar.⁸

Before undertaking this grant some work believed to be of considerable theoretical importance to this effort had been published by other workers in parallel fields.

II. Literature Survey

The results of a literature survey of the physical and chemical properties of the three ingredients are reported by substance.

A. Sodium Bicarbonate

White monoclinic prisms of a density 2.22 to 2.6 which when heated to 110-124° C lose H₂O and CO₂ in accordance with the following equation $2\text{NaHCO}_3 \longrightarrow \text{Na}_2\text{CO}_3 + \text{H}_2\text{O} + \text{CO}_2$ ($\Delta H = 20.3 \text{ kcal}$). When dissolved in water the bicarbonate ion hydrolyzes as follows: $\text{HCO}_3^- + \text{H}_2\text{O} \longrightarrow \text{H}_2\text{CO}_3 + \text{OH}^-$. Due to the limited solubility of CO₂ in water (0.04 moles per liter at 25° C) the H₂CO₃ decomposes to give CO₂ and H₂O. The CO₂ then escapes from the equilibrium thus converting more of the HCO₃⁻ to OH⁻. The OH⁻ formed reacts with the remaining HCO₃⁻ to give CO₃⁼ and H₂O and in this way almost all of the HCO₃⁻ in water solution is converted to CO₃⁼. Larger crystals of NaHCO₃ can be grown by evaporating the water from a solution of it kept saturated by a stream of CO₂.²⁸ The energy of activation for its thermal decomposition is reported to be 37.5 kcal/mole in the initial phase and to be autocatalyzed by CO₃⁼.³² Another report states that the Ea of decomposition is but 10.8 kcal/mole and that the CO₃⁼ has no effect.³³

It has been used as a fire suppressant but also is reported to lower the ignition temperature of cellulose fiber, paper and charcoal.³⁵

Its crystal structure has been determined³⁰ and shown to differ markedly from other salts. The HCO₃⁻ ion has C_{2v} symmetry (excluding

the H) with C-O bonds = 1.346, 1.264 and 1.263 Å in length. It is strongly hydrogen bonded similar to the dimers of the carboxylic acids. These H bond distances between adjacent HCO_3^- ions are 2.595 Å. Because of these strong H bonds it displays marked anisotropy in its coefficient of thermal expansion.

Its crystallization properties can be improved by adding small quantities of anionic detergents to the solution such as dodecetyl sulphonate.

Its reaction with SO_2 gas proceeds steadily up to 110° at which point the speed of this reaction increases several fold.

It is much less stable to heat than its congeners e.g. the dissociation pressure of NaHCO_3 at 100° is 650 mm compared to 50 mm for KHCO_3 and 10 mm for RbHCO_3 .

Epinfanov and Kunin⁶² report that dry SO_2 over a fluidized bed of NaHCO_3 reacts very slowly but at 110° the reaction velocity increases very rapidly.

B. Sulfur

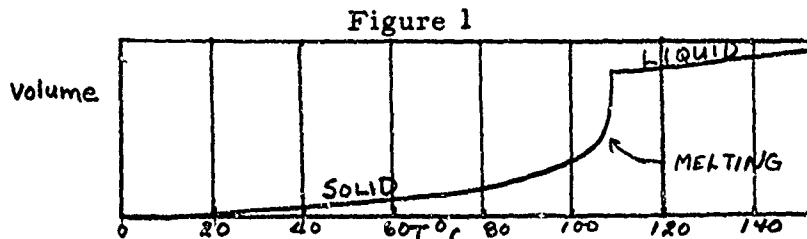
Perhaps the most succinct characterization of sulfur is given by B. Meyer³⁴ in which he states "The behaviour of sulfur is complex and capricious and can only be reproduced under well defined conditions". Every student of elementary physical chemistry is familiar with the phase diagram for sulfur but this of course is not nearly the full story.

The most pertinent (to this research) data about the chemical properties of sulfur is summarized below.

Ordinary rhombic sulfur exists as octagonal S_8 staggered rings sixteen of which are packed into a unit cell (orthorhombic)³⁵ of size $10.4 \times 12.8 \times 24.4$ Å. By making some rough approximations an average distance between S_8 molecules can be calculated at about 8 Å. A very much more reactive form of sulfur S_6 can be made and kept with special handling. Powdered sulfur exposed to air at ambient temperatures undergoes continued oxidation to SO_2 and if impregnated on charcoal this effect is speeded up. Its ignition temperature in air is 261°C ($257 - 264$ in O_2). The reaction is said to be autocatalytic and takes place in absence of light. The E_A for rupture of S-S bonds at 300° is calculated to be 27.5 kcal/mole but one explanation of some experimental results proposed two different types of sulfur atoms on the surface, one of which had an E_A of 37.5 kcal vs the other of 27.5.

The presence of CO_2 during oxidation of sulfur causes the reaction to be shifted toward SO_3 . The volume change on heating is quite striking (Fig. I) in the $100-110^\circ$ range. This is conclusive evidence for consider-

able crystal lattice loosening and thereby enhanced reactivity during this expansion of the atomic volume.



Its melting point is 112.8°C and its boiling point is 444.6°C . West³⁶ in very careful work with 99.99% purity material gave $T_m = 115.21$.

$$\text{The } \Delta S_{\text{melting}} = \frac{14,900}{386} = 39^- \text{ cal/mole degree}$$

$$\text{The } \Delta S_{\text{vaporization}} = \frac{11,580}{718} = 11.6 \text{ cal/mole degree}$$

This shows a great increase in randomness with melting as well as showing that the liquid is so random that there is much less increase when proceeding from the liquid to the gas.

(Trouton's Rule $\Delta S_v = 21.0$) $2S_3$ to $S_6 + S_2$ Thermochemical Values are for $S + O_2 \longrightarrow SO_2 \Delta H = -69$ and $2S + 3O_2 \longrightarrow 2SO_3 \Delta H = 92$

C. Potassium Chlorate

A survey of over one hundred references was made. Again what is believed to be the more pertinent data is given below.

Potassium chlorate colorless monoclinic crystals of a density of 2.32 melt at 368.4°C ^(*) and decompose at $400 - 500^{\circ}\text{C}$ according to the literature. The differential thermal analysis data from CRDL and this work show the melting point to be $350 \pm 3.2^{\circ}\text{C}$. depending upon the purity of the sample, heating rate and particle size. The decomposition of $KClO_3$ to KCl and O_2 has a calculated $\Delta H = -135.6 \text{ k cal/mole}$.

During its thermal decomposition paramagnetic susceptibility measurements are quite irregular indicating that the $KClO_3$ is converted into reaction products through transition intermediates that have unpaired electrons.⁴³ However, when various catalysts are used such as MnO_2 , NiO , CuO , etc. an infrared study⁴⁶ showed initial decomposition

According to Simchen¹⁹ $KClO_3$ has no congruent melting point because during heating it begins to decompose as a solid and causes either an obvious change in composition or the KCl acts as a flux.

temperatures as low as 200° C. An extensive study of the catalyzed decomposition was performed by Solymosi and Krix⁴⁷ and activation energies were calculated to be approximately 25 k cal/mole compared with 54 kcal/mole for the uncatalyzed reaction.

The infrared investigation of molten KClO_3 by Wilmshurst⁴⁹ showed an "ordered liquid" with lattice like vibrations apparent in the melt. This is not found to be the case with KClO_4 which can rotate freely about its threefold axis of symmetry.

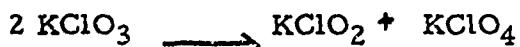
According to Rocchiccioli²⁹ the ClO_3^- ion is a skewed pyramid in which the Cl atom is not on the perpendicular bisector of the three oxygen atoms making up the triangular base.

According to Ellern³⁸ KClO_3 in its pure state disproportionates after melting as follows:



Glassner and Weidenfeld⁵⁰ suggested that the formation of the KClO_4 during the thermal decomposition should be due to a transfer of an oxygen atom from ClO_3^- to Cl^- . Vanden Bosch and Aten⁵¹ decomposed NaClO_3 in the presence of labeled NaCl which if Glassner and Weidenfeld were correct should result in the formation of labeled ClO_4^- . No labeled ClO_4^- was found and thus the mechanism of G & W was not confirmed.

Another mechanism^{54, 55} was postulated by some Japanese investigators in which an unshared pair of electrons leave the Cl^- and go to an oxygen atom.



Osada⁵⁶ based upon some analytical work postulated the following



in which reaction (2) predominates at lower temperatures.

Some work has been done on measuring the conductivity^{64, 65} of KClO_3 pellets but most of it is either rather old and/or incomplete for thermal decomposition work.

A tremendous amount of work has been done on modifying the crystal structure of KClO_3 by altering the nature of the solvent. H. E. Buckley^{66, 68, 69, 70} has published extensively on this aspect and the patent literature⁵⁸ is replete with usage of various dyes and detergents for making pronounced changes in morphology and claimed special

reactivities. $KClO_3$ can be crystallized as extremely thin lamellae long needles or almost spherical nodules. This is said to be of great importance to its performance in the match industry.⁶⁷

Latimer, Schutz and Hicks⁷¹ measured the heat capacity and entropy of $KClO_3$ from 13° to 300° K and found the $S^\circ 298.1 = 34.17$ entropy units.

D. Mixes

Although the thermal decomposition of $KClO_3$ is complex enough, mixtures of $KClO_3$ and oxidizable materials is still more so. For example Shidlovskiy⁵ states "mixtures of chlorates with sulfur exhibit very high degree of chemical instability and are capable in certain cases of spontaneous deflagration."

An apparent anomaly is also much discussed in the literature. It is that there is general agreement that the decomposition temperature of $KClO_3$ catalysed with MnO_2 , CuO , Co_2O_3 , etc. can be lowered from the neighborhood of 400° to $200-220^\circ$; yet attempts to add such catalysts in smoke and signal compositions in order to accelerate thermal decomposition have never met with any success in increasing the linear burning rates.⁵

There is a preignition reaction with $KClO_3$ and carbon¹³ is virtually certain and it is believed to begin at about 225° C.

By far the best source of data on the properties of $KClO_3$ mixes is the above cited Shidlovskiy⁵. These data are contained in the following tables.

Table 1: SELF IGNITION TEMPERATURE
AND
FLASH POINT FOR BINARY MIXTURES

Composition of Mixture in %	Self Ignition Temp. °C	Flash Point °C
$KClO_3$ - 86 Iditol - 14	345	510
$KClO_3$ - 63 Magnesium - 37	540	670
Colored Smoke Mix ($KClO_3$ -Sugar)	200	195

Table 2: RUBBING SENSITIVITIES

Oxidizer	Reducant	Sensitivity to friction in kg/cm ²
$KClO_3$	$K_3Fe(CN)_6$	8
$KClO_3$	KCNS	22
$KClO_3$	Lactose	60
$KClO_3$	Sulfur	65
$KClO_3$	$K_4Fe(CN)_6 \cdot H_2O$	85
$KClO_3$	Sb_2S_3	90

Table 3: DETONATION SPEED

Oxidizer	Reductant	% Reductant	Density	Det Speed m/sec
KClO ₃	Charcoal	13	1.27	1620
KClO ₃	Graphite	13	1.44	500
KClO ₃	Sulfur	28	1.36	1600

Table 4: See Appendix (1)

Another fruitful source for data on the behaviour of KClO₃ in various compositions is Ellern,³⁸ who states "the lower decomposition temperature and lower melting point (as compared to KClO₄), its exothermic thermal decomposition, the fact that this decomposition is easily catalyzed and the instability of free chloric acid are all factors which contribute to the greater reactivity and sensitivity of the chlorate mixtures.

The thermal decomposition of KClO₃ to KCl liberates 10.68 kcal/mole according to Circular 500 NBS⁷⁶.

Taradoire⁷⁴ gave the following ignition temperatures for sulfur mixes with various chlorates:

Pb(ClO ₃) ₂	63-67° C
AgClO ₃	74° C
Ba(ClO ₃) ₂ · H ₂ O	108-111° C
KClO ₃	160-162° C

Pertinent to the proposed mechanisms is that potassium chlorite (KClO₂) can be made by reduction of KClO₃ with oxalic acid. AgClO₂ decomposes readily into the chlorate and chloride,⁷⁸ and that the dried salt detonates at 105° when rubbed up with flowers of sulfur. The parent gas ClO₂ detonates on contact with sulfur.

The maximum reaction temperature of KClO₃ and sulfur may be calculated after Shidovskiy's approximation method to be 850° C.

Patal⁵² has published some work which seems to prove that LiCl is a catalyst for the C + KClO₃ reaction. Bakelite + KClO₃ with LiCl ignited after 2-3 minutes at 390°. Without LiCl the mixture was but 40% reacted in five hours.

Taradoire^{79, 80} found that a drop of H₂SO₄ on 0.5 g of a KClO₃ sulfur mix caused an explosion due to both HClO₃ and heating effects. Also he determined that SO₂ gas produced an explosion with KClO₃ + S at 100°.

III. THEORETICAL

A. Hedvall Effect and Tammann Temperature

First of all was the work by J. A. Hedvall,⁹ the godfather of solid state chemistry, which is now generally called the Hedvall Effect.

If it is assumed that with rise in temperature the atoms or ions in a crystal execute vibrations of continually increasing amplitude about their average position in the lattice, and when the amplitude of these vibrations becomes great enough, diffusion is enhanced and the particles can exchange positions. This results in a phase change; solid state transition at lower temperatures and melting at still higher amplitudes and temperatures. While a solid substance is undergoing a transformation of this type the atoms are in a "loosened" state and are much more reactive than in either crystalline form. This hypothesis is called the "Hedvall Effect". Hauffe²⁷ in his book "Reaktionen in und an festen Stoffen" states "the presence of lattice disturbances promotes reactions since place exchange processes are greatly facilitated." Also "solid substances in which there is great disorder and which are often very much loosened by the presence of channels, internal surfaces and other effects of 'micro-structure' are generally especially reactive."

A rough method of establishment of degree of "loosening" is by the Tammann¹⁰ temperature α which is the ratio of the absolute temperature of an ionic solid to its melting point also in °K. Thus surface mobility becomes active at about $\alpha = 0.3$ and lattice diffusion requires an α of 0.5 or higher.

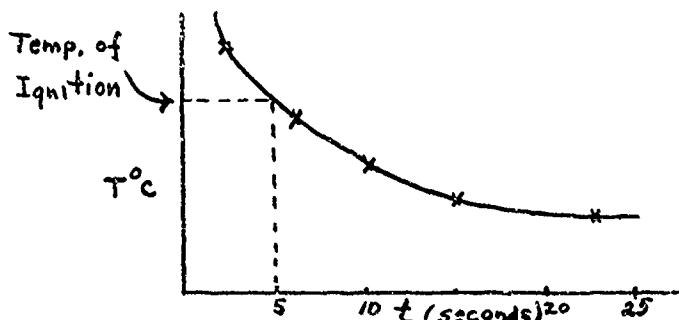
B. Preignition Reactions

Of considerable importance to the theory of solid state chemistry is the work of Spice and Stavely^{11, 12, 45}, "The Propagation of Exothermic Reactions in Solid Systems". These authors discovered in pellets of the systems Fe - Ba O₂ and Fe - K₂ Cr₂ O₇ the existence of what they called a 'preignition reaction' characterized by discoloration, cracking and swelling. These reactions were proven to be genuine solid-solid reactions and their role in propagation of the incandescent reaction was discussed.

It is interesting to note that the Ba O₂ - Fe pellets which showed this reaction at about 300° C range or 573° K. The melting point of Ba O₂ = 400° C or 673° K thus α (Tammann temp.) = $\frac{573}{673} = 0.85$ well in excess of the required 0.5 for lattice diffusion. Ignition temperature for the reaction = 345-350° C.

The K₂ Cr₂ O₇ (T_m = 968.3) - Fe System had a PIR which sets in at about 350° C or 623° K and an α = $\frac{623}{1241} = 0.502$. Its ignition temperature as nearly as could be determined was approximately 380° C.

Ignition temperature is something which deserves some comment. The standard method of determination is the old Woods metal bath, blasting cap tube containing the sample and stop watch. A plot of temperature of ignition as ascertained visually with time is made and the five second time is decreed to be the ignition temperature. (Fig. 2) Obviously such a method must depend upon the coefficient



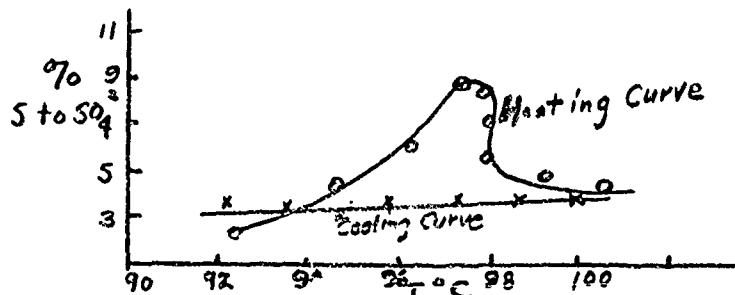
of thermal conductivity of the ingredients, their specific heats, the amount and other factors and is very often misleading when attempting to ascertain the ignition sensitivity of a given mix to primer flash or to first fire ignition. Ignition temperature can be defined as that temperature to which enough mass of reactants must be raised so that the heat given off by the reaction exceeds the heat lost by an amount necessary to heat the adjoining reaction layer to this required temperature. Thus there is a kinetic factor involved because if the amount reacting is either very small or if it takes a relatively long time to react radiation and convection losses outweigh the heat conduction to the next layer and propagation of the reaction fails. It is possible of course to "ignite" these types of reactions properly but then have propagation failures about half way through the burning column because of too much loss of heat.

It is believed that the P.I.R. s discovered by Spice and Stavely are in fact identical to the so-called incandescent reactions but at the lower temperatures their rate is so low that the amount of heat generated per unit time is not enough to heat the next layer to ignition. Patai and Hoffman^{13,52,53} mixed $KClO_3$ with various reducing agents (carbon black, paraffin, starch and asphalt) and determined that these mixtures when heated at relatively low temperatures undergo an exothermal pre-ignition reaction with an E_a for $KClO_3 - C = 13.5$ and $KClO_3 - Asphalt = 11.0$. These authors stated that the P I R is the important step for propagation because of the heat it supplies which then raises the temperature of any given layer to its ignition point. It is believed that here as well the P I R is the same reaction as the incandescent reaction but proceeding at a rate so slow as to be practically offset by heat losses. For the mix in question this layer-layer mechanism or heat conduction mechanism can be complicated by the phase change involved, or to be explicit the ignition temperature or activation energy necessary to start the $S - KClO_3 - NaHCO_3$ mix at ambient temperatures is in all probability quite different than the E_a for the reaction when any sulfur next to the reaction zone reaches 95.5° the temperature of its phase change and the ensuing Hedvall effect.

For true solid-solid reactions the velocity depends upon

- (1) Extent and activity of the surface
- (2) The transport of matter through the reacted product
- (3) Supply of reactive particles from the interior of the reactants to the reaction zone

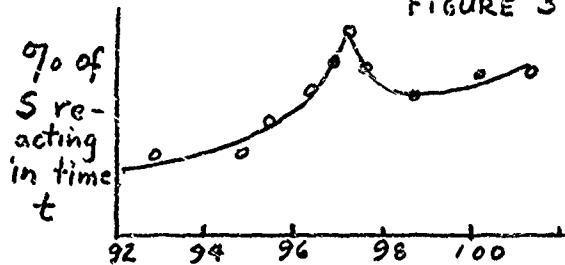
Experimental evidence for this in the case of sulfur has been found by Hedvall¹⁴.



For the oxidation of sulfur in acid KMnO_4 in a range of temperatures bracketing the transition point results were obtained as shown in Fig. 1. Interestingly enough when the reaction is started at higher temperatures and allowed to cool the results were as shown by the cooling curve. This difference can be explained by realizing that the transition from rhombic to monoclinic is an abrupt one whereas the reverse monoclinic to rhombic is extremely slow.

Additional experimental evidence in confirmation of this are vulcanization velocity experiments with pure sulfur and rubber (Hedvall, *Ibid*) as shown in Fig. 3.

FIGURE 3



Whether or not local "hot spots" occurring during pressing or in heat up due to SO_2 or SO_3 evolution during storage of the sulfur-chlorate fuel mix approach these temperatures is debatable.

C. Hot Spot Theory

Perhaps something should be said here about the "Hot Spot" theory of explosion of Ubbelohde,¹⁵ Ubbelohde and Woodward,¹⁶ Bowden¹⁷ and others.

Exothermic decomposition reactions have a higher temperature inside the mass of the reactants than on the surface. If it is assumed that the rate of decomposition increases with temperature according to

$$k = A e^{-E/RT}$$

then a steady state cannot be maintained if the heat loss is too small. For if the heat loss is too small the reaction becomes self heating until its rate reaches explosive velocities. The condition for transition from a thermally stable steady state to explosive velocities by self heating is (Ubbelohde & Woodward, *ibid*) where $d = 1/2$ thickness

$$\frac{E_a}{RT_0^2} \frac{(d^2 W)}{(K)} \left(A e^{-\frac{E_a}{RT}} \right) \geq 0.88$$

of disc of reactants

K = thermal conductivity

$W = Q/P$ heat of the reaction per unit volume

Because of this self heating phenomenon special care must be taken with solids which decompose with the evolution of heat ($KClO_3$ for example).

Upon examination of the above equation it can be seen that the minimum mass for departure from steady state to explosion velocities is markedly affected by Q and E_a . For some reactions Q and E_a may (Ubbelohde in Garners "Chem. of the Solid State"¹⁸) be so large as to allow very small masses to run away to explosion. This aspect is desirable in initiating explosives. On the other hand when an explosion is not desirable considerable care must be observed in order to prevent the heating up of even very tiny volumes of the reactants ($1 \times 10^{-3} - 10^{-5}$ cm diameter).

Studies on detonation sensitivity of explosives have shown percussion or friction leads to localization of heat evolution called "hot spots". Addition of grit particles or of bubbles in liquid explosives causes greatly increased sensitivity because if their temperatures rise above the critical limit they in turn grow into the surrounding reaction mass causing detonation. The hot-spot picture is more or less the thermal analogue of the concentrations of mechanical stresses about nicks in a steel spring which causes fatigue failures.

Sometimes decomposition products provide a liquid phase (fuel mix in this problem) and because reactions can proceed much faster in the liquid phase than in the solid this will have a pronounced effect on the kinetics, and as has been stated previously it is not necessary to have melting to produce autocatalysis. It is only essential that the original lattices be loosened or disordered enough to permit adequate diffusion and growth of new lattices. As decomposition proceeds the area of interface between the two lattices which is often highly disordered increases rapidly at first and since the rate is proportional to this area autocatalysis may set in and cause explosion.

Growing decomposition rates due to the production of a crystal-crystal interface or to the presence of a reactive phase such as liquid

sulfur generally exhibit an induction period before thermal decomposition proceeds at appreciable rates at any specified temperature. The length of time of these induction periods is related to the temperature at which they are measured by $\ln t = B - E/RT$. Thus for the run away reaction to extend into the reactant mass the temperature of a small mass or volume of reactant or hot spot must be maintained for a longer time than the induction period for that mass at that temperature.

The system under study in this research is believed beyond doubt to be a self heating mechanism and that runaway reactions or explosions result from thermal imbalance. The induction period should follow the Arrhenius relation stated above. This could be verified by experimental determination of induction time in a similar manner to the ignition temperature experiments described previously.

D. Physical Picture of Reaction Mechanism for $\text{KClO}_3 + \text{S}$ System

It is well known that in reactions in solids unlike reactions in liquids or gases the participating reactants are not available under conditions defined by simple statistical laws. By definition the motion of the particles making up the crystalline lattice is restricted to very small vibration amplitudes about a mean low energy position unless at very high temperatures. This of course is particularly true about the interior units of the lattice and less true about the surface units which are but "partially" bonded and possess larger amplitudes than those in the interior at comparable temperatures.

If two intact crystalline lattices are placed adjacent to each other a reaction can proceed which yields a product which in itself is solid. Depending upon the chemical nature, molecular volume, etc. of this product layer the reaction may proceed by allowing the reacting units to diffuse through it.

The importance and direction of influence of the rate controlling parameters such as surface area, contact area, diffusion rate, defect structure of both reactant and product and temperature is obvious.

There are two ways that particles may be transferred through a macro crystalline mass of product.

- (1) Diffusion through the normal crystal lattice of the product.
- (2) Diffusion along crystal surfaces, fissures, cracks, pores in imperfectly crystalline material.

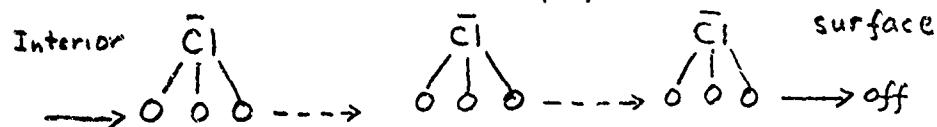
It may seem to be merely academic to discuss solid-solid reaction theory in this report for almost certainly the ignition temperature of the fuel mix is in excess of the melting point of sulfur. But, as has been stated previously, sulfur is "both complex and capricious" and solid-solid theory can be quite pertinent for two reasons:

(1) If the reaction has a pre-ignition reaction a la Spice and Stavely or Patai and Hoffman which is known to be a true solid-solid reaction.

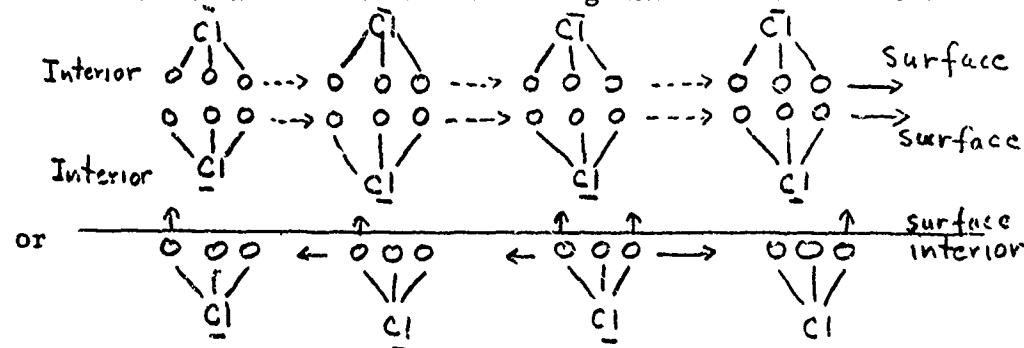
(2) If sulfur after melting does stay in its "Roman phalanxes" of shielded covalent octagonal rings which allows the eight membered ring mobility but does nothing (or very little) to enhance the reactivity of a sulfur atom.

Sulfur and potassium chlorate should have a pre-ignition reaction for Δ (Tammann temperature) for sulfur = 0.5 at 195° K and Δ for KClO_3 = 0.5 at 324° K.

One possible mechanism is similar to the decomposition of KClO_4 postulated by Simchen¹⁹ which involves the diffusion of oxygen ions toward an electron rich system between ions of the lattice and/or defects of the lattice or diffusion through cracks and fissures of the macro-crystals. Also the oxygen can proceed by jumps from ClO_3^- to ClO_2^- formed at the surface. See reference (56).



The irregular crystal structure of KClO_3 skewed pyramid which is reported to undergo a transition from monoclinic to ortho rhombic above 250° ^{29, 57} and give a unit cell twice as large as when monoclinic seems to favor attack by oxygen atoms on sulfur with the postulated jump mechanism. For one an oxygen atom leaves the surface its neighbor is then highly activated and will also react and leave. This is the start of a fissure or channel something like the sketches below



and again the vacant lattice sites will be replenished from the surface, grain boundaries and finally interior of the crystal.

E. Magnesium Oxide and Doping

Part of the literature survey included the old project notebooks at Chemical Research and Development Laboratories.²⁰ In notebook

1232 some data was found on burning rates of colored smoke grenades which had some added MgO and/or MgCO₃. These mixtures gave excellent smoke emission but the burning rates were roughly six times as fast for the same quantity of material. No explanation was found for this phenomenon in the notebooks but it was believed that it was worth investigation in the course of this work and if MgO is truly a catalyst for this burning reaction it could function by lowering the decomposition temperature of the KClO₃. This would result in a reduction of the ignition temperature, thickening of the reaction zone and thusly a major increase in burning rate. The effect of MgO or KClO₃ decomposition may give an effective clue as to the mechanism.

Some previous T G A work by E. Freeman and D. Anderson²¹ on thermal decomposition of KClO₄ has shown that MgO is an excellent catalyst for this reaction. Inasmuch as it is relatively certain that KClO₄ goes through KClO₃ on its way to decomposition to KCl and O₂ it is believed that this work was important. The results of Freeman and Anderson's work may be summarized as follows:

If the temperature at which 50% of the KClO₄ was decomposed = T°C, the temperature for 50% decomposition of the following mixtures is as shown

KClO ₄ - Mg	T-28°
KClO ₄ - MgO	T-52°
KClO ₄ - MgO (unrad)	T+8°

In another experiment in which the KClO₄ was mixed with three different magnesium oxides it was shown that the lowest temperature of decomposition occurred with MgO doped with 1 mole percent of Li₂O, next with pure MgO and highest with MgO doped with 1 mole percent of Fe₂O₃.

It was postulated that the important factor in the mechanism of decomposition of KClO₄ is the transfer of electrons from the perchlorate to positive holes in the valence band of the oxide. Thus any treatment decreasing positive holes in the oxide should decrease catalytic efficiency. Irradiation by μ -rays caused a measurable increase in density of MgO probably due to some decomposition and an increase in interstitial magnesium ions with a consequent annihilation of positive holes and decrease in catalytic efficiency of the irradiated oxide.

Also the doping results substantiate this postulate since Fe₂O₃ doping decreases positive holes and Li₂O doping increases them.

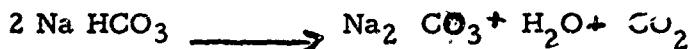
Some other work by Hogan, Freeman and Anderson²² showed that doping of KClO₄ with Cu⁺⁺, I⁻ and Ag⁺ had a pronounced effect on the Mg - KClO₄ reaction. I⁻ doping causes the decomposition temperature of the KClO₄ to be reduced to 494° C from 526° C. Cu⁺⁺ doping reduced

the decomposition temperature to 492° C. "Both of these doped compositions were very much less ignitable than the compositions containing pure KClO_4 ." This is explained by the authors as due to essentially complete decomposition of the perchlorate before the temperature at which magnesium becomes reactive is reached.

F. Role of Moisture

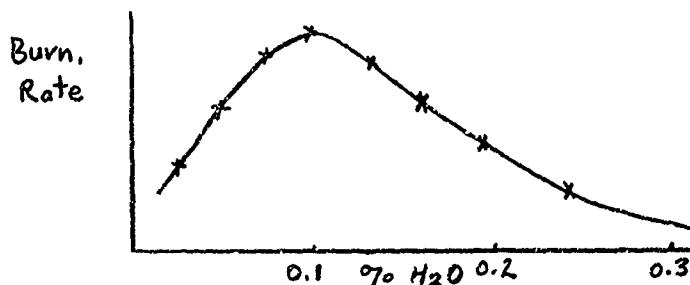
The importance of water molecules being vaporized in the course of the burning reaction cannot be under-emphasized. In their escape from the reaction zone and the pre-ignition zone they are bound to cause erosive and fissuring effects on the KClO_3 macro-crystal.

In practice the moisture level of all ingredients is kept to practical minimum of 0.1%. After mixing the moisture level certainly is not decreased and 0.1% by weight of 360 g of mix = 0.36g of H_2O . 0.36g of H_2O when in the vapor state = 580 cc of H_2O vapor which will of course equilibrate itself throughout the entire mix in the approximate 550 ml of mix in the loaded grenade. It is to be expected that there will be water molecules available to all portions of the reactant mass certainly after ignition and near the reaction zone. Residual moisture is perhaps the least important source for if the ignition temperature of the fuel mix is greater than 124° C which is the highest temperature of decomposition of the sodium bicarbonate.



then every mole of bicarbonate yields a half of a mole of H_2O gas and even allows a slight 'cooking' period in the region of mix below the reaction zone. Water vapor could then act as a crystal lattice 'unzipper' and would greatly facilitate KClO_3 breakdown into fissures, cracks and faults.

The role of water vapor as an accelerator in pyrotechnic reactions is well recognized if not as well understood. An outstanding case is the flare compositions in which it has been ascertained that rate of burning and color quality are markedly dependent on very small changes in moisture content.²³ (See Fig. 4.)



A similar phenomenon has been observed by A. Wetterholm of Nitroglycerin A. B. Gyttorp Sweden²⁴ with electric blasting cap delays using lead peroxide and ferro silicon. Because of static hazards these millisecond delays are loaded in a humidified atmosphere into hermetically sealed units. After three days storage the burning rates are as much as 25% greater.

G. Mechanical Treatment

It has been the practice of some contractors as well as Government loading installations to keep their potassium chlorate in a drier building and then micropulverize it almost immediately before mixing. It is just possible that this may contribute to any hazard involved in the mixing and loading operations.

Naeser and Scholz⁴³ and Gregg⁶⁰ who make the obvious assumption that reactions involving solids are influenced by the condition of the lattice of the solid have given conclusive experimental evidence that mechanical treatment does lower ignition temperatures and speed up reaction. Some examples from Naeser and Scholz are

a. Reaction temperature of milled Fe_2O_3 and SiO_2 was $150^\circ - 200^\circ$ lower than in unmilled mixture of same particle size.

b. CuO milled reacts with H_2 at $200^\circ C$ and the unmilled reacts at $240^\circ C$.

c. Cr_2O_3 milled for several hours was put side by side with an unmilled sample and hydrogen gas passed over them at $1250^\circ C$. The milled Cr_2O_3 was reduced to chromium metal the unmilled stayed a green powder.

An example from Gregg is Kaolin the reactivity of which is greatly enhanced by prolonged grinding.

X-ray evidence does show much lattice loosening in these more or less hard crystals.

H. Oxidizer Comparisons

It has been demonstrated many times with star compositions in commercial pyrotechnics that other oxidizers than $KClO_3$ such as KNO_3 , $KClO_4$, NH_4ClO_4 give a "washed out" color value due to the higher temperatures obtaining in the burning reaction. This effect can be partially remedied by using chlorinated hydrocarbons, but the best colors by far are always obtained with $KClO_3$ compositions.

It is also true that colored smoke compositions in which $KClO_4$ is substituted for $KClO_3$ are very poor as to volume and color of the smoke. This should mean that $KClO_3$ is the important member of the $S + KClO_3$ reaction and does much to govern its temperature of ignition and propagation. Consequently any major modification of these properties for the reaction should involve alteration of the $KClO_3$.

I. Possible Applications

Assuming that it can be shown that the mechanism does involve a ClO_3^- break down with or without the aid of H_2O , diffusion along cracks and attack on a reactive S_3 fragment or that it is closely similar to this

picture then as a practical matter what can be done about it?

Sulfur role - With its multifarious phase changes and transitions at comparatively low temperatures several approaches suggest themselves.

(1) Doping

(a) Selenium to replace at least one of the eight sulfurs in the octagonal ring.

(b) Postpone or eliminate one or more of the phase changes with Pb, Sn, SnS, SnS₂, Fe, etc.

(c) Coat sulfur macro crystals with a temperature stable (up to a point) colloid or macro molecule.

(d) Use sulfur compounds as fuel.

Potassium Chlorate role ---

(a) increase induction period by coating with guar, PVA, CMC, dextrin, gum arabic, etc.

(b) Change crystalline habit

(1) doping

(2) Solvent alteration

(3) Coating

(c) Catalysts

(1) MgO

(2) MnO₂

(3) Mo, 2no et al

(d) Phlegmatizers

(1) Gums, dextrines et al - Analogous to dextrinated, PVA coated, CMC coated lead azide.

Sodium Bicarbonate role ---

Doubtful that it is any more than a coolant but it may act as a flux by providing CO₂ and H₂O vapor.

DTA of S + KClO₃ vs. DTA of S + KClO₃ + Na HCO₃ should suffice to determine its effect on the burning reaction.

III. EXPERIMENTAL PROCEDURES

Ultimately any approach to determination of the effect of solid phase or liquid for that manner on the rate sensitivity, storage stability et al of this fuel mix system comes down to the experimental techniques available and applicable.

Four techniques suggest themselves as applicable:

- (1) Differential thermal analysis - DTA
 - (a) Thermogravimetric analysis - TGA
- (2) Crawford Bomb
- (3) Conductivity studies
- (4) Burning rate studies

A. Differential Thermal Analysis (DTA)

The theory and applicability of DTA measurements to exothermic reactions is well known³⁹ and any explanation here would be redundant. The principle of the method is that it measures fairly accurately the temperature differences between a sample and a reference material. The DTA data should not be confused with data from a differential calorimeter which is designed to measure energy differences and not temperature differences. DTA data is applicable without question as to what temperature a given transition ensues but the depths and breadths of the peaks or troughs can do nothing more than give the experimenter an intelligent guess as to energy input or output. All DTA data in this report were obtained on a duPont 900 Differential Thermal Analyzer.

It should be mentioned that there is one serious disadvantage to DTA in that the runs are made on unconsolidated mixes. The apparent density of the compact is known to play a profound role on the reaction rates and in all probability the ignition temperatures. Another disadvantage is if the heat output is small. More will be said later about this.

Thermogravimetric analysis (TGA) has not been as widely used, indeed it is not as widely applicable as is DTA especially on rapid burning or explosive systems.

The experimental program for DTA measurements was designed to give transition temperature information on the following:

- (1) Sulfur commercial and purified
- (2) Na HCO₃ commercial
- (3) KClO₃ commercial
 - (a) moisture effects
- (4) Sulfur doped with 1 to 2%
 - S - Pb
 - S - Se
 - S - Cr Cl₃
- (5) KClO₃ doped, coated, recrystallized from solutions of surface active agents.
 - (a) Doped
 - i. KClO₃ from 1% KMnO₄ solution

2. KClO_3 from LiClO_3 solution
3. KClO_3 from Ba ClO_3 solution
4. KClO_3 from Ag ClO_3 solution
5. KClO_3 + catalysts (MgO , MnO_2 , NiO , etc.)

(b) Recrystallized from solutions of surface active agents

1. Dreft
2. Methyl orange
3. Tide
4. Congo red

(c) Coated

1. Crystallized from gum arabic
2. Crystallized from dextrose
3. Crystallized from PVA (Elvanol)
4. Crystallized from Guar
5. Crystallized from Na carboxy methyl cellulose

(6) Pairs of ingredients

- (a) KClO_3 + S with moisture effects
- (b) KClO_3 + Na HCO_3
- (c) S + Na HCO_3

(7) Triplets of ingredients

- (a) Specification KClO_3 , S, Na HCO_3
- (b) Specification KClO_3 , S, Na HCO_3 + MgO
- (c) Specification KClO_3 , S, Na HCO_3 + MgCO_3
- (d) Specification KClO_3 , S, Na HCO_3 + SiO_2
(Cabosil Silocel)

(8) P. I. R. onset in the following systems to correlate with conductivity data

- (a) PbO - Si
- (b) Pb_3O_4 - Si
- (c) $\text{K}_2\text{Cr}_2\text{O}_7$ - Fe
- (d) BaO_2 - Fe

B. Crawford Bomb

Strand burning tests in a Crawford Bomb are used exhaustively in propellant development laboratories to determine the pressure temperature coefficient. Although it was known or felt that all $KClO_3$ compositions have high P-T coefficients it was believed advisable to find out just how high because these values really define the extent of hazard involved when accidental ignition occurs during press loading and to a smaller but real extent when emission holes become clogged with ash and tar during the functioning of the munition.

C. Thermoconductimetric Analysis

All conductivity data in this report were obtained with the use of a General Radio Co. Electrometer Type 1230A and a voltage of 9.1 \pm . An elementary schematic diagram of the instrument is shown below in Figure 5.

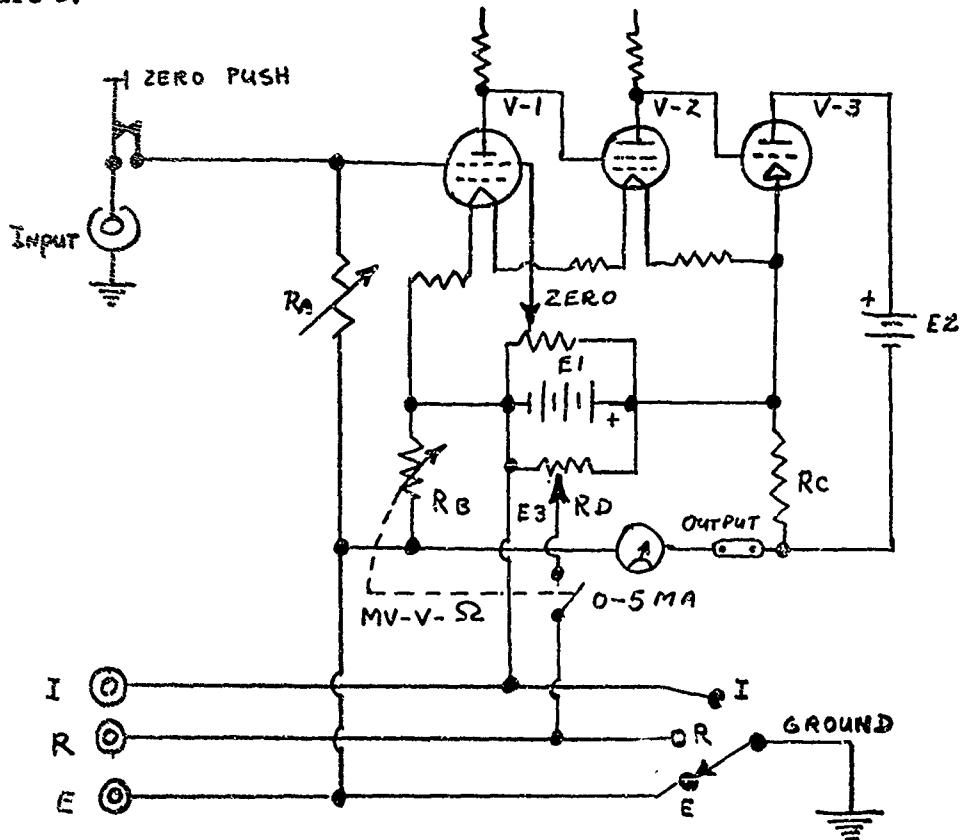


FIGURE 5 - Elementary Schematic Diagram for Type 1230-A D-C Amplifier and Electrometer

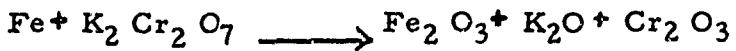
The limits of the instrument are 1×10^4 - 1×10^{11} ohms.

The fundamental basis for the use of conductivity measurements as an investigatorial tool for solid state reactions rests on the Einstein

diffusion coefficient - conductivity relationship, $\frac{6}{D} = \frac{Ne^2}{kT}$. Thus inasmuch as reactivity depends upon diffusion rates and diffusion rates are proportional to conductivity for similar defects then reactivity must be proportional to conductivity.

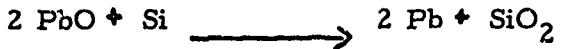
Another type of use of conductivity measurements is their application to systems in which there is a wide variation in electronic conductivity between reactants and products. Two examples of this are

1. Spice and Stavely mixes



where the extent of reaction can be measured by the decrease in conductivity of the reactants as they are changed to products.

2. Normally poor conducting reactants forming good conducting products



Conductivity measurements are also important as an experimental test for detecting the presence of a liquid phase or of any transition in pure solids.

A survey of the literature has revealed that although DTA and TGA and conductivity measurements are used extensively in the subject area they are used more or less independently and there has been little or no work done attempting to correlate and develop the two experimental methods, as experimental supports for each other. The development and amplification of application to solid state chemistry of conductivity measurements was one of the important objects of this work. The fact that conductivity measurements are made on pelleted materials is believed to be important. Also it was believed that the application of conductivity measurements to thermal analysis was completely new with this work. It was not until early in 1965 that we learned of a somewhat parallel effort by Jen Chiu⁴¹. However, as nearly as we could determine Chiu was not planning on pelleting the material. One other reference to conductivity as a tool for thermal analysis of solid-solid reactions was by Berg and Burnistrova⁸¹ who combined the two methods. The previous neglect of this technique of thermal analysis is typified by noting that in 434 pages of the latest reference work³⁹ approximately two pages are devoted to conductivity. However instruments for this application have been described by Reisman et al⁸² Shimizu⁸³ and others.³⁹

The conductivity cells used in this work were of the following designs and were placed into a nichrome wire coil on pyrex tubing asbestos coated oven for heating. (See Figure 6). All conductivity measurements were made on pelleted materials. Pressures of 25000 psi and upward were used for consolidation. In some cases a vacuum fitted pelleting die was necessary to get crack free pellets.

D. Burning Rate Studies

In the so-called gasless delays such as $\text{PbO} - \text{Si}$, $\text{Fe}_2\text{O}_3 - \text{Ti}$, $\text{Ba} - \text{Cr} - \text{O}_4 - \text{Zr}$, etc. the burning time of a column of uniform cross section is quite sensitive to the condition of the ingredients. This is true of HC types C, D and E Smoke mixes which have burning times essentially dependent upon the purity and previous history of the zinc oxide.²⁶ Also, burning times (and quality of smoke) was the control method used during the development of the smoke grenades and on which there is considerable previous data.

It was deemed advisable to see if burning times of fuel mix could be obtained which were of such a constant nature as to allow small changes in constituents to be reflected in burning rate data.

Times were taken with a manually operated stop watch calibrated in 0.01 second intervals.

A limited amount of work was done with pellets but they varied so much in burning characteristics that the data was discarded.

Some lengths of 1/8" galvanized iron pipe were cut into 10 cm lengths, reamed, deburred and degreased. These were loaded at varying pressures under pressure from a 0.250" ram on a laboratory press. Initiation was provided by McLain Starter²⁵ but this, because of its slag forming properties, gave different degrees of obturation during the burning, creating different pressures and variable burning rates. Nichrome heating element wire was also used for ignition but this too was not entirely satisfactory.

Eventually we standardized on a method of burning as follows:

The loaded tube was clamped upside down from its loading position in an asbestos covered test tube clamp mounted on a ring stand. A small length of "Quick Match" was bent about 1/2" from one end and this bent end inserted upward into the loaded tube in contact with the mix. The long end of the quick match was ignited and timing was started when the mix was ignited. This method allowed any molten reaction products to drip from the tube and gave excellently reproducible results.

The results of the burning rate studies will be found in V, C. of this report.

V. RESULTS

A. DTA

Approximately fifty runs were made on the ingredients and mixtures. The results of those which were pertinent to the discussion are reproduced in Appendix 1, Figures 7, 8, 9, 10, 11, 12, 13, 14 and 15, 17, 19, and 21.

B. TCA

After a great deal of difficulty in achieving reliable temperature measurements and ridding ourselves of stray current problems, approximately thirty conductivity measurements were made. The results pertinent to this discussion are contained in Appendix 1, Figures 16, 18, 20, 22 and 23.

C. Burning Rates

The data obtained are summarized in the following tables:

No.	Composition	Loading Pressure	Density	Burning Rate		Remarks
				mm/sec	mg/sec	
1 2 3 4 5 6 7 8 9 10	70% stoichiometric KClO ₃ +S v. in 30% NaHCO ₃	500 lbs dead load	?	1.61	?	No. 's 1 thru 4 burned much faster be- cause of ob- turation from slag starter. Ignition by quick match only. w/obturation
				1.50	?	
				1.47	?	
				1.54	?	
				2.08	1.00	
				2.04	1.05	
				2.02	0.94	
				2.09	0.96	
				1.97	0.99	
				2.05	1.03	
Av			2.04	1.00	68	averages on #5-10 only

No.	Composition	Loading Pressure	Density	Burning Rate		Remarks
				mm/sec	mg/sec	
1	KClO ₃ 71.4%	500 lbs.	2.02	0.76	51	Difficult to ignite, but burned smoothly when started
2	S }	dead load	1.99	0.75	49	
3	NaHCO ₃ 14.3%		1.87	0.78	48	
4	MgCO ₃ 14.3%		2.04	0.71	48	
5			2.02	0.74	49	
Av.			1.99	0.75	49	

No.	Composition	Loading Pressure	Density	Burning Rate		Remarks
				mm/sec	mg/sec	
1	68.6% stoichio-metric, Sulfur-KClO ₃ mix	500 lb. dead load	2.05	0.95	64	
2			2.08	0.91	63	
3			2.05	1.01	69	
4			2.00	1.06	70	
5			2.04	1.02	68	
Avg.			2.04	0.99	67	

*Confirms Shidlovskiy
Energy of activation needs to
be done.

No.	Composition	Loading Pressure	Density	Burning Rate		Remarks
				mm/sec	mg/sec	
1	58% stoich. KClO ₃ - S	500 lb. dead load	2.00	1.07	70	
2	30% NaHCO ₃		2.05	1.11	75	
3	12% MgO		2.29	1.46	97	Difficult to ignite. Surged badly during burning. One propagation failure.
4			1.99	1.03	67	w/ McLain starter
Avg.			2.08	1.17	77	

No.	Composition	Loading Pressure	Density	Burning Rate		Remarks
				mm/sec	mg/sec	
1	70% Stoich. KClO ₃ - Sulfur	500 lb. dead load	2.09	0.88	61	
2	30% NaHCO ₃		2.16	1.02	72	
Avg	Sulfur Contained 1% CrCl ₃		2.12	0.95	66	
3	70% Stoich. KClO ₃ - Sulfur		2.00	1.09	72	
4	30% NaHCO ₃		2.07	1.11	76	
Avg	Sulfur Contained 1% Selenium		2.04	1.10	74	

Burning times for various coated KClO_3 mixes. All mixes are 70% Stoichiometric Sulfur- KClO_3 , 30% NaHCO_3 .

No.	Coating	Loading Pressure	Density	Burning Rate		Remarks
				mm/sec	mg/sec	
1	Rosin	500 lbs. dead load	1.79	1.01	60	
2	Rosin		1.99	0.97	64	
3	Rosin		2.03	0.98	66	
Avg.			1.94	0.99	63	
4	Guar	500 lbs. dead load	2.10	0.98(0.97)	68(67)	two timings
5	Guar		1.98	1.06(1.05)	70(69)	two timings
6	Guar		2.02	1.04	70	
Avg.			2.03	1.02	69	Average of 5 burning times
7	Stearic Acid	500 lbs. dead load	1.98	0.90	59	Very smooth
8	Stearic Acid		1.90	0.89	56	
9	Stearic Acid		1.97	0.95(0.94)	62(61)	two timings
Avg.			1.95	0.92	60	Average of 4 burning times

Burning time data for various doped Chlorates. Mixes were all 70% Stoichiometric KClO_3 - Sulfur, 30% NaHCO_3

No.	Doping Material	Loading Pressure	Density	Burning Rate		Remarks
				mm/sec	mg/sec	
1	KIO_3	500 lb. dead load	2.05	1.04	70	
2	KIO_3		2.04	1.02	68	
Avg.			2.045	1.03	69	
3	BaClO_3	500 lb. dead load	1.97	1.05	68	
4	BaClO_3		1.91	1.17	74	
Avg.			1.94	1.11	71	
5	KBrO_3	500 lb. dead load	2.06	0.92	63	
6	KBrO_3		2.03	1.00	67	
Avg.			2.045	0.96	65	
7	KClO_4	500 lb. dead load	2.03	1.04	70	
8	KClO_4		1.80	1.03	61	
Avg.			1.92	1.035	66	

No.	Composition	Loading Pressure	Density	Burning Rate		Remarks
				mm/sec	mg/sec	
1	70% Stoich.	500 lb.	1.99	1.52	99.9	
2	KClO ₃ - Sulfur	dead load	2.01	1.25	83.1	
3	8.4 MgO		2.04	1.26	85.0	
4	21.6 NaHCO ₃		2.06	1.33	90.3	
5			1.96	1.62	104.7	
Avg.			2.01	1.40	92.6	

Additional Observations -- After having learned that the loaded tubes burned much more reproducibly without slag starter and by ignition from the bottom end so that the molten end products did not cause a pressure build up it was noticed that the end of the burning time could be predicted by the appearance of the top layer of composition.

The approach of the combustion zone is heralded by a gradual darkening of the cream colored mix to yellow orange and brown orange. This darkening starts from the periphery of the tube and works its way in toward the center due undoubtedly to the conductance of heat down the inner wall of the tube. That burning does take place faster on the outside edge is confirmed by the observation of the flame front on the outside edge sometimes to such an extent that the last two or three millimeters of mix burns as a floating pellet; top, bottom and circumference.

On the slower burning mixes sulfur fumes appear the sulfur melts and bubbles before incandescence makes its appearance. Burning times from appearance of dark orange to completion varied from 1.4 sec. to 3.6 sec. for the fast and slow respectively. Combustion zone widths were 2.2 mm to 3.6 mm. in thickness.

D. Supersensitive Potassium Chlorate

Potassium chlorate was dissolved in distilled water and 2.8 mole percent of Cu(ClO₃)₂ · 6H₂O was added to the solution. The excess water was distilled off under oil pump vacuum at a temperature of 65-70°C.*

* Cu(ClO₃)₂ · 6H₂O decomposes at 100° C.

The residual light blue laminar crystals were then dried for twenty four hours in an oven kept at $68^{\circ}\text{C.} \pm 1^{\circ}$.

1.23 g of the dried doped chlorate was mixed with 0.48 g of purified sulfur by grinding gently in an agate mortar with an agate pestle behind a barricade. The pulverized mixture was placed in a 10 ml. plastic capped glass vial and allowed to stand behind the barricade. After approximately thirty minutes a detonation occurred pulverizing vial and cap and giving burn marks on the table surface.

This experiment was repeated with same amounts of the same substances about one week later except that the materials were added to the vial before mixing. Mixing was done by tumbling the vial for approximately ten minutes about its major axes. After approximately twenty four hours of standing behind the barricade, a similar detonation occurred. Observation of the mixture obtained by tumbling did show that it did not approach the degree of homogeneity obtained by mixing in the mortar. This was to be expected because of the size of the crystals which must be broken down to get good mixing.

E. Analytical Results

1. Analysis of Smoke from Burning Rate Tubes --

SO_2 obvious from odor.

Some smoke was collected in a flask and analyzed qualitatively. Results were Cl^- , SO_3^- positive HCO_3^- trace, H_3O^+ and Na^+ positive.

2. Analysis of residue in burning rate tubes showed Cl^- , $\text{SO}_4^{=}$, Na^+ , K^+ and OH^- all to be present.

3. Analysis of KClO_3 pellet after conductivity measurements from 30°C to 315°C. (63)

After the above treatment a pellet was analyzed for KClO_3 and found to be only 98.9% KClO_3 . That some decomposition had taken place is also borne out by the photograph of the pellet after heating on page 75.

4. Analysis of $\text{Cu}(\text{ClO}_3)_2$ doped KClO_3 .

The KClO_3 doped with $\text{Cu}(\text{ClO}_3)_2 \cdot 6\text{H}_2\text{O}$ prepared as described in Section III, E. was analyzed for ClO_3^- , Cu^{++} , Cl^- , ClO_2^- , and H_2O moisture.

Results were:

ClO_3^-	66.3% (63)	98.1% of theoretical
ClO_2^-	trace only	for 2.6 mole %
Cl^-		$\text{Cu}(\text{ClO}_3)_2 \cdot 6\text{H}_2\text{O}$

H_2O moisture	2.54%
Cu^{++}	1.8% Cu^{++} or
	2.8 mole % $\text{Cu}(\text{ClO}_3)_2 \cdot 6\text{H}_2\text{O}$

* Colorimetrically as $\text{Cu}(\text{NH}_3)_4^{++}$ with Klett-Summerson Colorimeter.

5. Flame tests on synthetic chlorates.

AgClO_3 , LiClO_3 , $\text{Cu}(\text{ClO}_3)_2 \cdot 6\text{H}_2\text{O}$ were tested after filtration and recrystallization for the presence of Ba^{++} by means of a platinum wire. All but AgClO_3 were free of this ion and it was recrystallized repeatedly until it too was clear of Ba^{++} .

VI. DISCUSSION OF RESULTS

It is believed that this section can best serve its purpose if the data is discussed by category of experimental method, and emphasis should be placed upon only the data pertinent to the development of a reaction mechanism. Reliable but extraneous data to the reaction mechanism is to be only briefly cited and sometimes neglected entirely in this section. These data are of course able to be obtained from the figures included under Section V (Results) of this report.

A. D. T. A.

Reference is made to Figure 7 on which it can be seen previous history makes but a slight difference in the DTA plots of potassium chlorate. The melting points are quite reproducible, the exothermic decomposition does not occur until after melting and although the exotherms have a different structure they all set in but a few degrees higher than the melting point.

The effect of grinding the chlorate immediately before thermal analysis appears to be important, in that the DTA trace (No. 3, Fig. 7) shows a premelting endotherm and much more abrupt and complete decomposition giving evidence of lattice strain.

The effects of doping and coating KClO_3 are shown in Figures 8 and 9. The more important points to mention in these two are:

1. Figure 8

The KClO_3 from Congo Red shows two distinct exotherms one of them prior to melting. This could be due to oxidation of the dye by the more reactive chlorate ions (surface, corners, edges, fissures) and when these are used up melting has to occur to bring about the main body of the reaction. A similar exotherm occurs with the KMnO_4 doped material but not as striking.

The $\text{Cu}(\text{ClO}_3)_2$ doped chlorate however is hardly recognizable as a similar substance. Notice the beginning of a totally new exotherm ca 150°C , a pronounced premelting endotherm and the evidence that at 368°C decomposition is essentially complete. Also melting takes place at the very low temperature of 334° . All of these point to enhanced reactivity of this type of KClO_3 .

2. Figure 9

All of these show a premelting exotherm in contradistinction to pure KClO_3 . The most outstanding of these is the KClO_3 crystallized

from "Dreft" solution which was quite bizarre in its appearance (filamentous elastic monoclinic needles in nodules). These pre-melting exotherms may be due to oxidation of the coating or doping material or to a premelting exothermic decomposition of the more active ions. The S shaped curve is typical for solid state decompositions (See Garner).

3. Figures 10 and 11

Figure 10 is somewhat surprising in that there is considerable difference between the transition temperatures of the three samples, yet traces (1) and (2) run at CRDL by three operators with several different samples were quite reproducible. The literature values seem to be extraordinarily high even for example the boiling point.

Figure 11 which shows the DTA traces of two sulfur samples in which an attempt was made to modify behaviour by altering the electronic environment showed only one major change. That is the decreasing of the temperature of the to Π liquid transition point.

4. Figure 12

These data were plotted from the literature and there are two important observations (1) that the increase in heat capacity ensues at 135-140° and that maximum rate of conversion of Δ to Π form occurs at 159.1°.

5. Figure 13

These doped chlorates of which two are almost exactly like pure $KClO_3$ were included for two reasons:

- (1) Barium chlorate is a monohydrate and the long range of melting may be due to the effect of the water of hydration.
- (2) The $AgClO_3$ doped material showed the same premelting exotherm as other highly reactive forms of $KClO_3$. In a way this confirms Taradoires ignition temperature data.

6. Figure 14

These thermograms of the S- $KClO_3$ mix are highly important in that they show that the sulfur goes from rhombic to monoclinic and melts with no apparent effect on the $KClO_3$. Also they do show a pronounced preignition reaction (PIR) starting at 142°, 146° and 144°. (The freshly ground $KClO_3$ showed a PIR starting at about 122° in two parts, the second of which was the 144°). Furthermore, ignition (or runaway reaction rate) takes place at 158°, 154° and 151°.

7. Figure 15

Some more of S- $KClO_3$ mixes using modified $KClO_3$. Much the same PIR's were at 145°, 135° and 152°. Ignitions were at 154°, 167°.

and 172°. It should be mentioned that trace number (1); KClO_3 doped with KMnO_4 gave two PIRs separated by an obvious endotherm similar to but much more pronounced than the freshly ground material on Fig. 14. The first PIR was 122° in this case as it was in Figure 14.

8. Figure 21

Some NaHCO_3 and $\text{NaHCO}_3 + \text{S}$ thermograms which show
(1) Effect of storage on the NaHCO_3
(2) No reaction of S with NaHCO_3 in this temperature range.

B. Thermoconductimetric Analysis (TCA)

1. Figures 16 and 17

Here an attempt was made to correlate the DTA and the TCA apparatus. Although we did get sharp conductivity fall offs in TCA work at 285° and 335° as would be expected when the BaO_2 starts to react with the metallic iron powder the thermogram was disappointing in that we seemed to get reaction at 162°. Whether or not this is due to powdered samples in DTA versus compressed pellets in TCA is problematical. An encouraging result for TCA should be noted, however, and that is that in systems of low heat output the conductivity changes may well be a much more accurate measurement of thermal effects.

2. Figures 18 and 23

Figure 18 represents the data of TCA runs on four pellets of KClO_3 . Pellets A and B show extreme electronic mobility starting about 120° C. Pellets C and D show the usual "knee" for semiconductors starting about the same temperature. Pellets A & B showed gross evidence of melting and decomposition. Pellets C & D were unmarked. See the upper picture on Figure 23 for a comparison. The analytical data also confirmed that 14 % of the KClO_3 in pellets A and B had decomposed. It is possible that these pellets were of variable water content prior to measuring.

3. Figure 19, 20 and 22

This was work designed to confirm the conductivity measurements using the system ($\text{PbO} - \text{Si}$ 80-20) similar to the $\text{BaO}_2 - \text{Fe}$ work. The measurements on PbO do agree quite satisfactorily with literature results. The DTA trace and TCA trace are difficult to interpret.

C. Burning Rate Studies

Although these results are not yet complete, they are valuable for several reasons. For one thing the burning rate measurements have been proven to be reproducible to the extent that confidence can be attached to this procedure for evaluating both positive and negative catalysts to the system.

Secondly, magnesium oxide has been found to increase the burning rate sometimes as much as 60 to 70 percent. This confirms similar data in actual grenades obtained during initial development at Edgewood during World War II as well as fulfilling a prediction of Freeman and Anderson based on DTA data on $KClO_4$.⁽²¹⁾ Also magnesium carbonate has been found to slow the reaction to a measurable extent.

Lastly and of very real importance to the understanding of the reaction mechanism is the fact that although manganese dioxide is an excellent catalyst for potassium chlorate decomposition, it does not alter the burning rate of the fuel mix. This is in agreement with Shidlovskiy⁽⁵⁾ who in the following quotation does not quite say the same thing but means the same. On page 165 Shidlovskiy states: "Attempts to introduce such substances as MnO_2 and others into chlorate signal fire compositions to accelerate thermal decomposition of potassium chlorate have not met with success: the combustion rates of the preparations were not increased". The first clause is based upon the mistaken belief that the thermal decomposition of $KClO_3$ is necessary to the mechanism of burning. In fact, the literature confirms what every college freshman knows; that MnO_2 does "accelerate the thermal decomposition of $KClO_3$ ". The fact that MnO_2 does not accelerate burning rates can only mean that thermal decomposition of $KClO_3$ is not the rate determining step. In other words, caution should be exercised in attempting to correlate catalytic reactivity for thermal decomposition of $KClO_3$ to burning rates or sensitivity of the $KClO_3$ - S system.⁽⁸⁸⁾

D. Supersensitive Potassium Chlorate

Aside from the spectacular, the finding that a potassium chlorate could be made which when mixed with sulfur is spontaneously detonable at room temperature there are two byproducts of this experiment.

The doctrine of using brass, bronze or copper screens, tools and jigs for pyrotechnic mixing and loading for non-sparking properties certainly needs to be reexamined in light of these findings. Also just the very fact that the lattice of $KClO_3$ can be so loosened as to ignition at ambient temperatures does shed light on the reaction mechanism postulated in the following section.

VII. POSTULATED REACTION MECHANISM

After just one year's study it might seem presumptuous to even postulate a mechanism for the sulfur-chlorate reaction. However, data without reflection is mostly futile and more importantly experimentation during the continuation of this work will be more efficient if guided by such a postulate. Even if it is only possible to dispose of one alternative considerable advantage will incur and further design of experiment can be aided greatly.

One point should be made strongly before entering into the postulated mechanism and its confirmation. Data and that is that there is very little connection between the thermal decomposition of pure KClO_3 and the reaction of S and KClO_3 .

It is believed that as the KClO_3 - S mixture is heated the sulfur goes from S_8 rhombic to S_8 monoclinic, then melts to S_8 liquid. None of these transitions are of any real importance to the mechanism except as precursors for the next transition when the liquid S_8 molecules break down into S_3 (λ to π forms) fragments. Evidence for this temperature comes from West (see Fig. 12). Although the maximum in West's heat capacity curve does not occur until 159.1°C , the initiation of the Cp increase occurs at or above 140°C . It is obvious that S_3 will be much more reactive than S_8 because of electron availability, shape and size.

If now the S_3 fragments are able to penetrate the loose KClO_3 lattice or perhaps only erode it creating fissures or other imperfections reactions will ensue giving off heat, creating more imperfections and reactive sites which will grow in number until ignition occurs. It is believed the PIR as shown on the DTA traces is the reaction of S_3 fragments (in relatively small concentrations with surface potassium chlorate).

If this postulate is essentially correct the reaction should be fastest when the concentration of S_3 fragments is at its highest, and the onset of the PIR should begin at or near 140°C . Also the ignition temperature should be able to be influenced by changing the nature of the sulfur molecule and of course the structure of the KClO_3 crystal.

The results of experiments in these directions are contained in DTA and Thermoconductimetric plots. Figures 7 thru 19.

It should be noted that all DTA plots of S- KClO_3 mixes show that the P.I.R. starts at or slightly above the temperature at which S_3 fragments begin to appear. Also ignition points are always in excess of 150° . Taradoires⁽⁷⁴⁾ ignition temperatures 160 - 162°C .

Although DTA plots do not show solid state decomposition of KClO_3 (there is a possibility that drop in base line may be due to this) the results obtained on freshly pressed pellets under compression with brass electrodes do show decomposition, and enhanced reactivity. This decomposition was confirmed by analysis.

Also the important fact that MnO_2 and similar do not speed the burning rate is exceedingly important showing fairly conclusively that inasmuch as they are successful catalysts for the thermal decomposition of KClO_3 and the reaction under study is not influenced then this decomposition is not important to the mechanism.

Finally, the fact that an exothermic decomposition of KClO_3 can be induced before melting by fresh grinding or by suitable doping proves the role of the lattice faults in enhancing reactivity.

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Composition Pb_3O_4 54.2
Mn 11.6
Si 34.2
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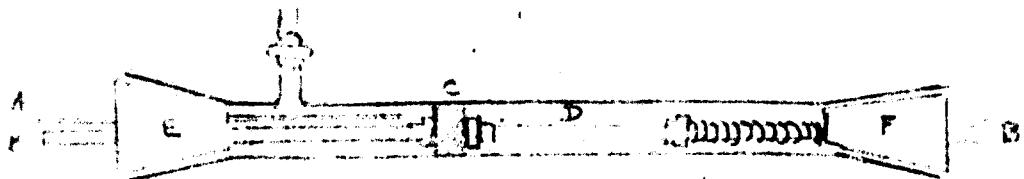
APPENDIX
Table 4
IMPACT SENSITIVITIES (5)

KClO₃ COMBINATIONS

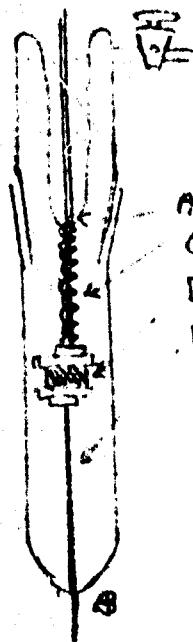
OXIDIZER	REDUCTANT	WORK OF IMPACT NEEDED FOR 50% IGNITION (KG·M/CM ²)
KClO ₃	K ₂ CO ₃	0.5
KClO ₃	As ₂ S ₃	0.6
KClO ₃	Sulfur	1.1
KClO ₃	Paraffin	1.1
KClO ₃	Naphthalene	1.3
KClO ₃	Lactose	1.8
KClO ₃	K ₄ Fe(CN) ₆	2.2
KClO ₃	Charcoal	3.5
KClO ₃	Mg (powdered)	4.5
KClO ₂	Graphite	10.0

SULFUR AND LACTOSE COMBINATIONS

OXIDIZER	REDUCTANT	WORK OF IMPACT
KClO ₃	SULFUR	1.1
KClO ₄	SULFUR	1.2
KNO ₃	SULFUR	3.6
KClO ₃	LACTOSE	1.8
KClO ₄	LACTOSE	2.9
KNO ₃	LACTOSE	5.0



A. Thermocouple well
 B. Electrodes
 C. Pellet
 D. Spring loaded electrode
 E, F. Stainless steel std taper plugs.



A, B Glass-tungsten seals
 C Spring loaded electrode
 D Pellet
 E, F Stationary electrode

Figure 6
 J. H. McL.

THERMOCOGRAM

100-141 mesh

- ① KClO_3 - RDL - Fischer Certified
- ② KClO_3 Army Spec Dried at 115°C for 72 hrs.
- ③ KClO_3 " " "
- ④ KClO_3 Ground for 20 minutes just prior to run.
- ⑤ KClO_3 Same as ① except run is one day later.

APPENDIX

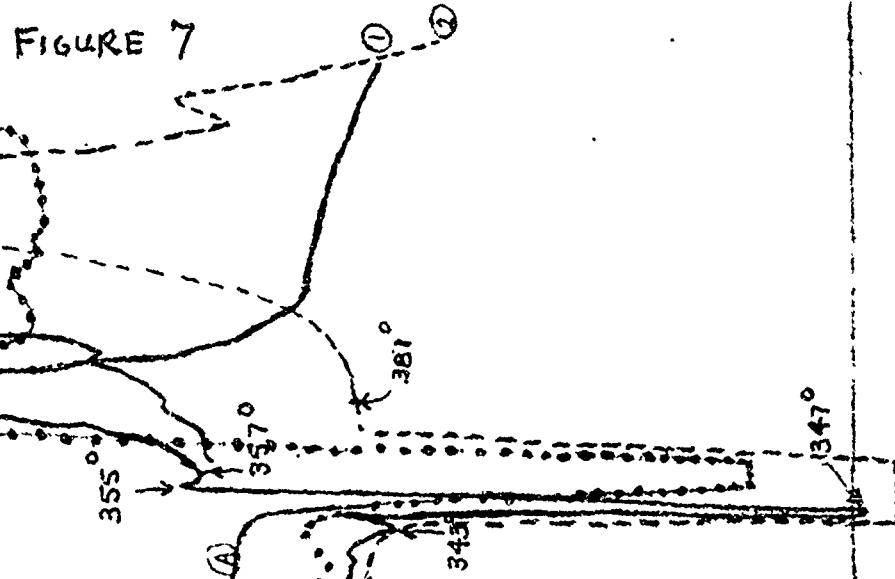
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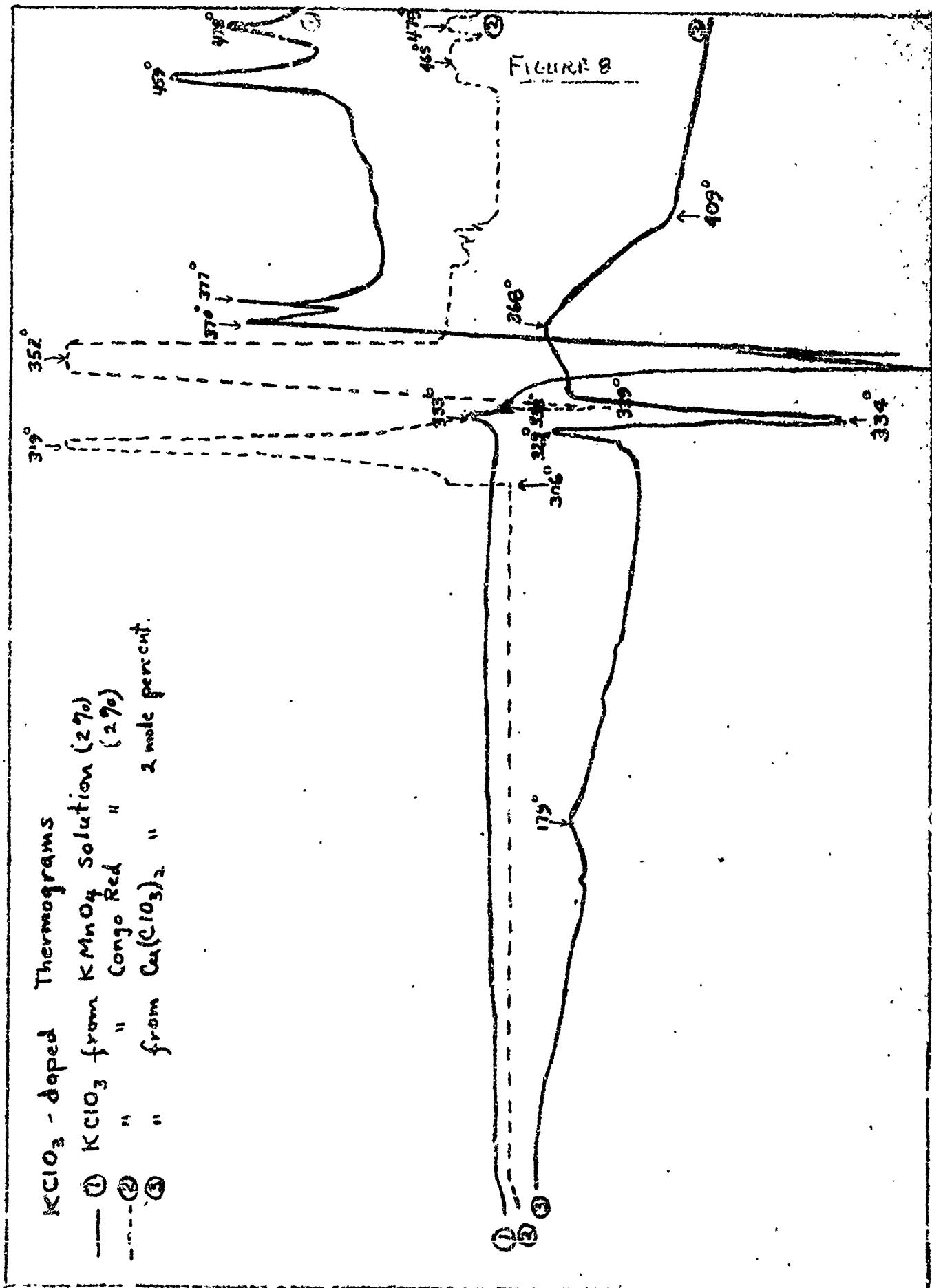
EXO ←

ΔT →

Endo

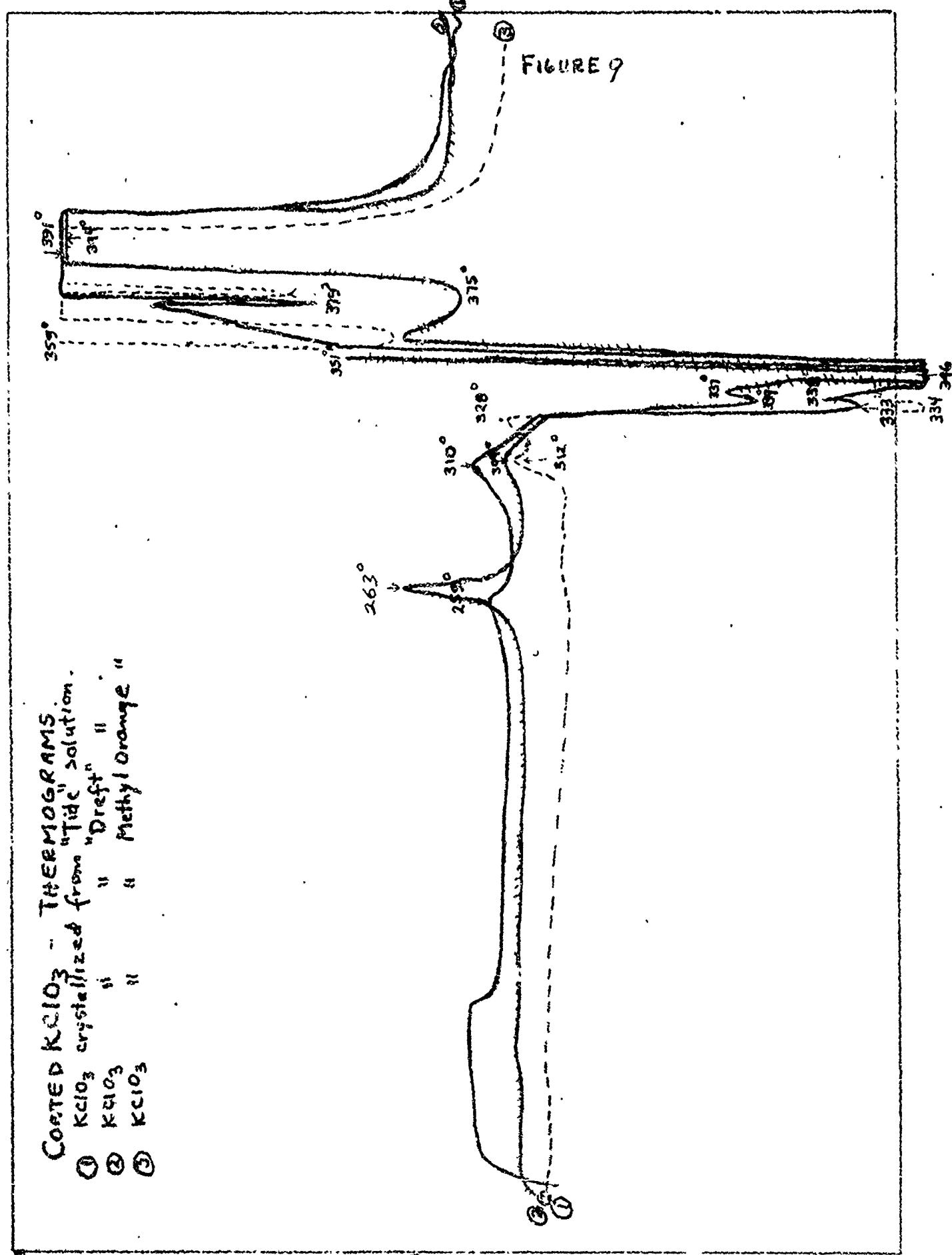
FIGURE 7

 $T^\circ\text{C} (\text{CHROMEL-ALUMEL})$



A-98

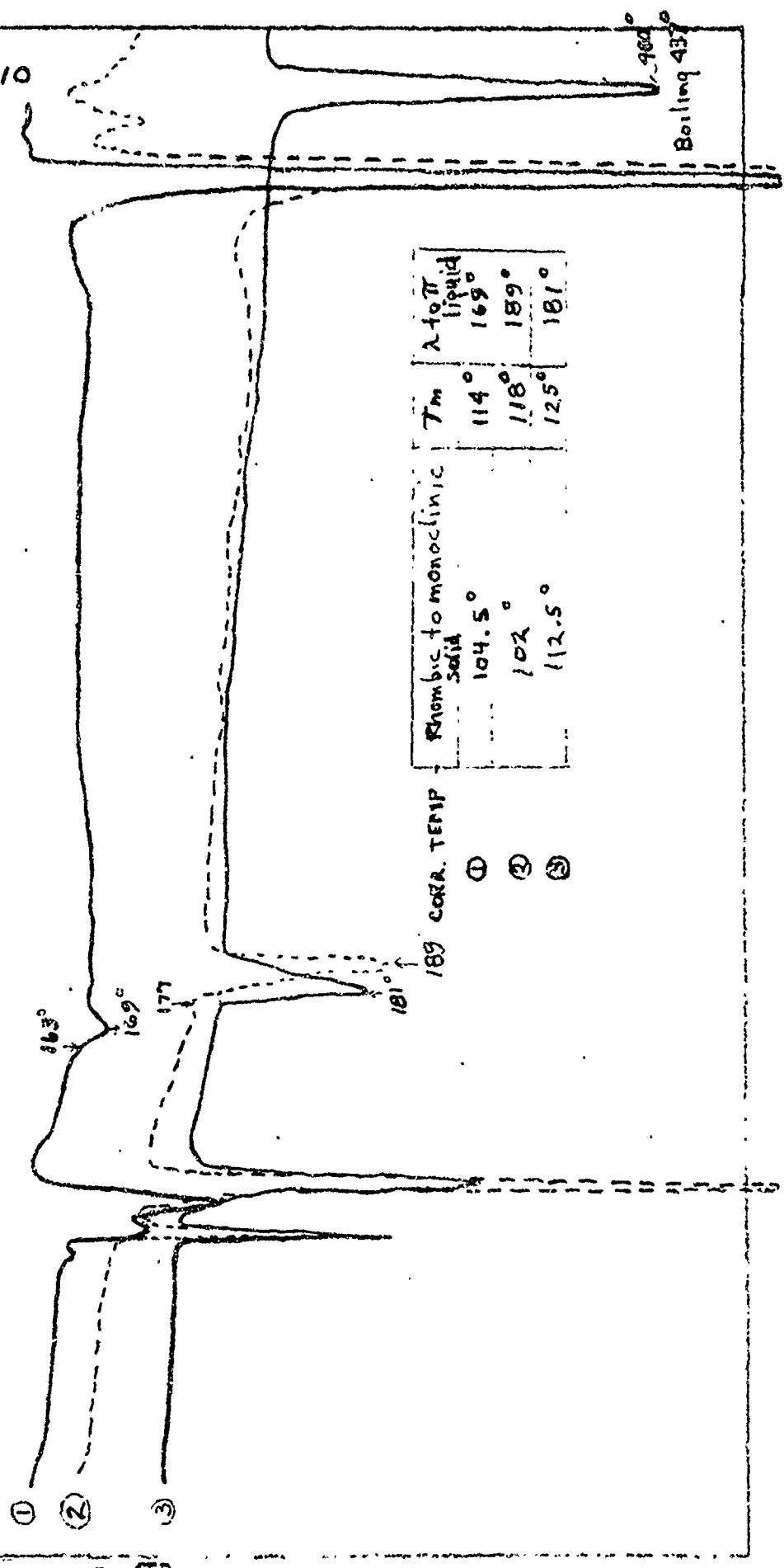
APPENDIX

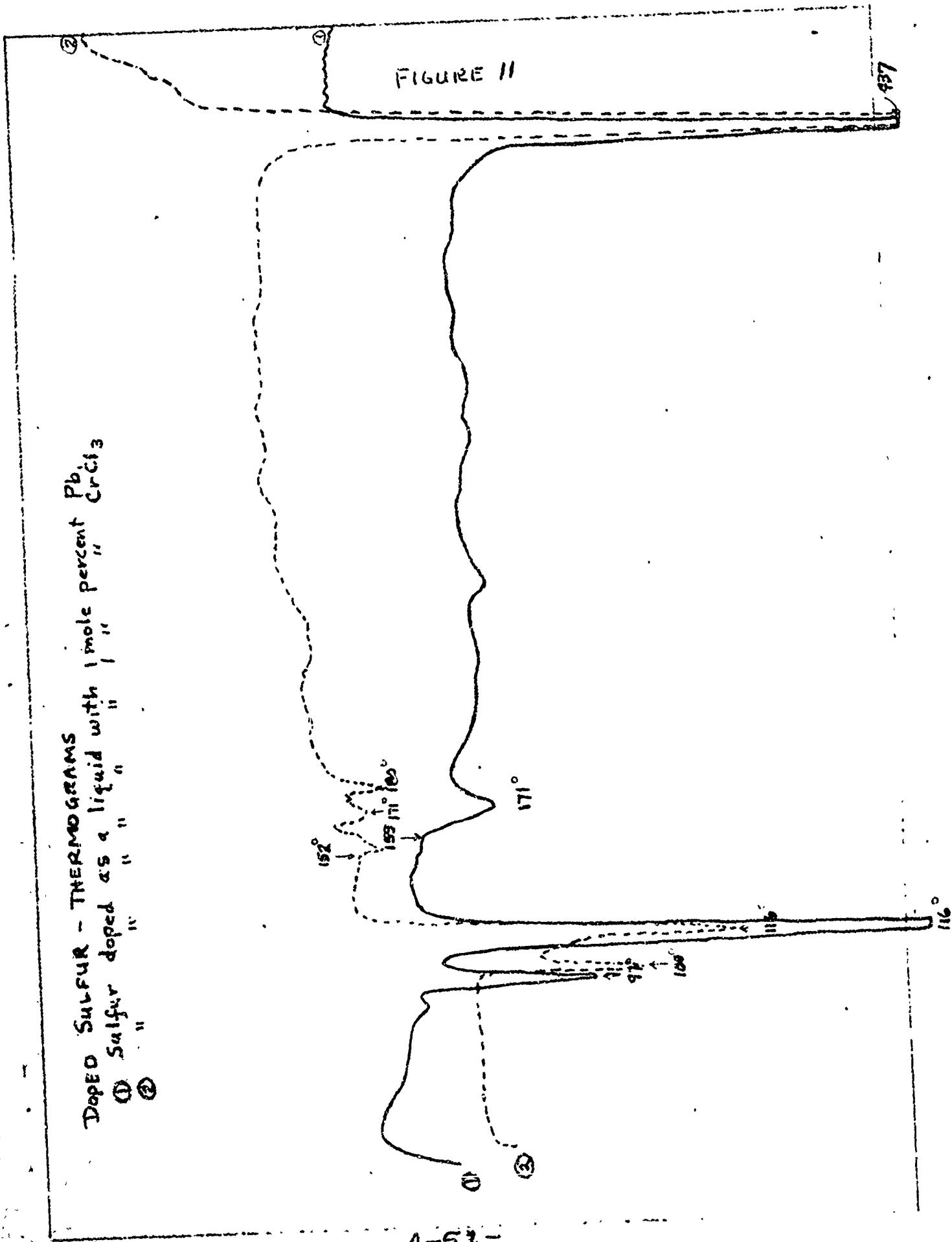


SULFUR THERMOGRAM.

- ② Before purification
- ① After
- ③ Literature

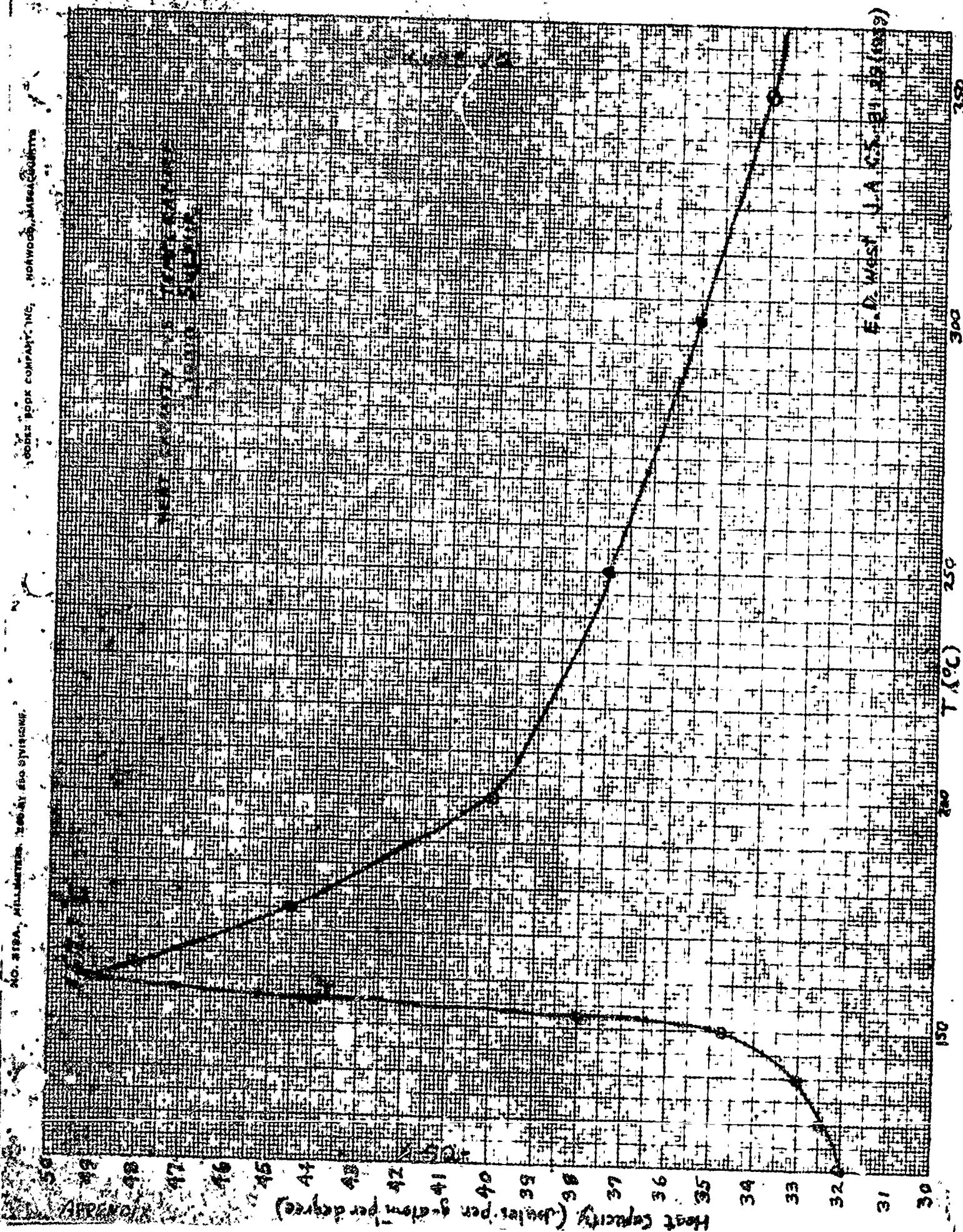
FIGURE 10





APPENDIX

A-51-



Doped $KClO_3$ THERMOGRAM
 ① $KClO_3 + 2$ mole percent $KClO_4$
 ② $KClO_3 + 2$ " " $BaClO_3$
 ③ $KClO_3 + 2$ " " $AgClO_3$

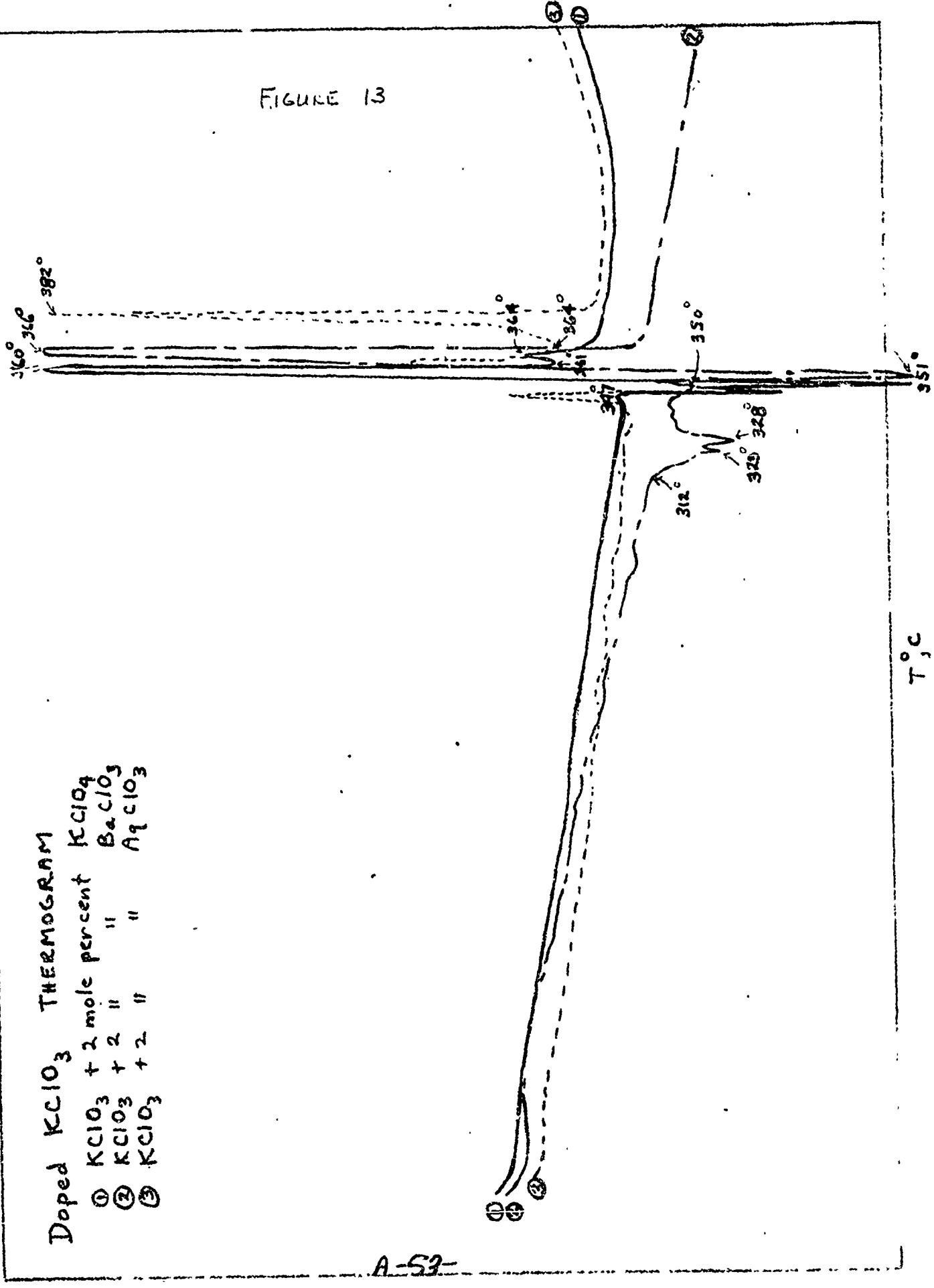


FIGURE 14

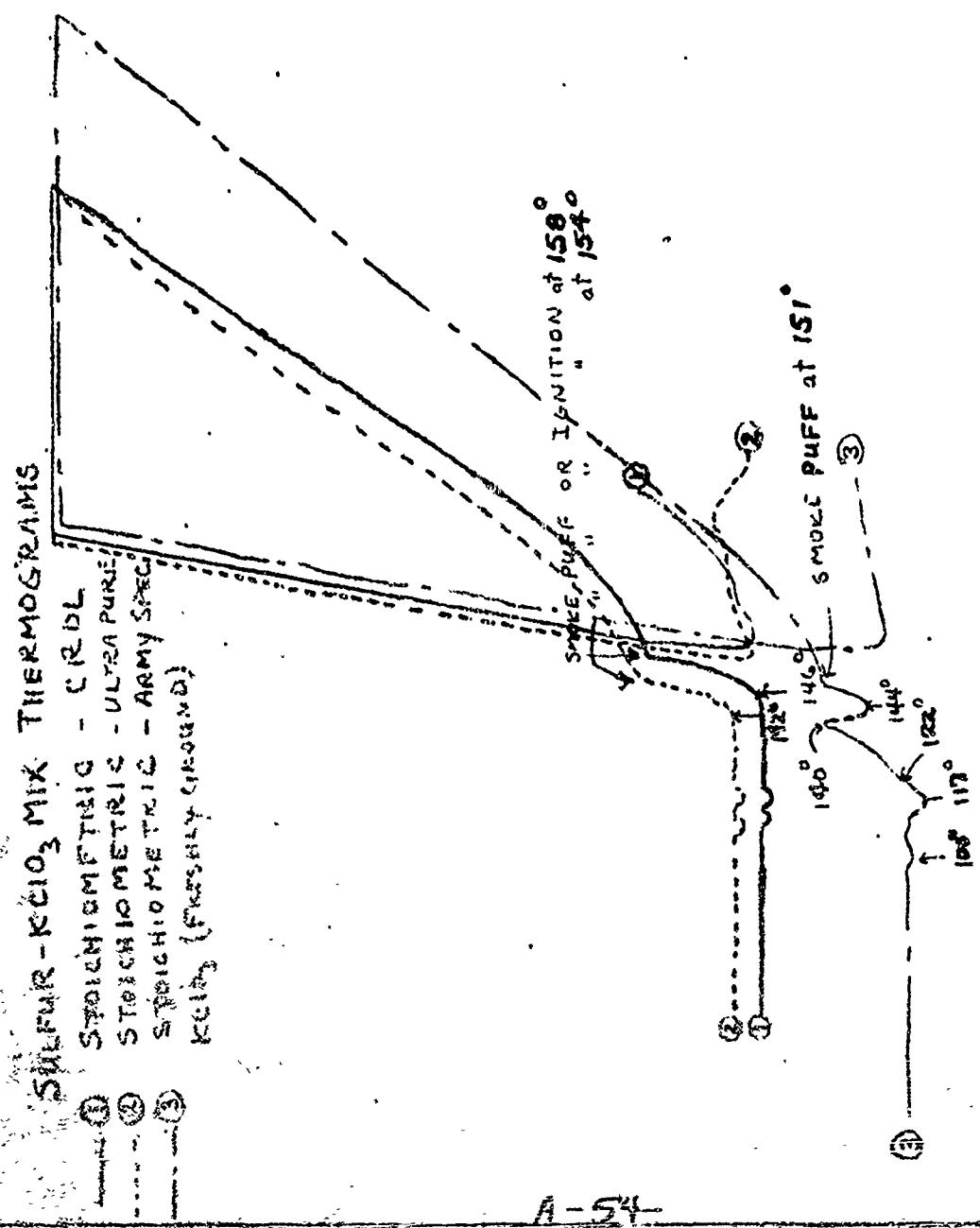
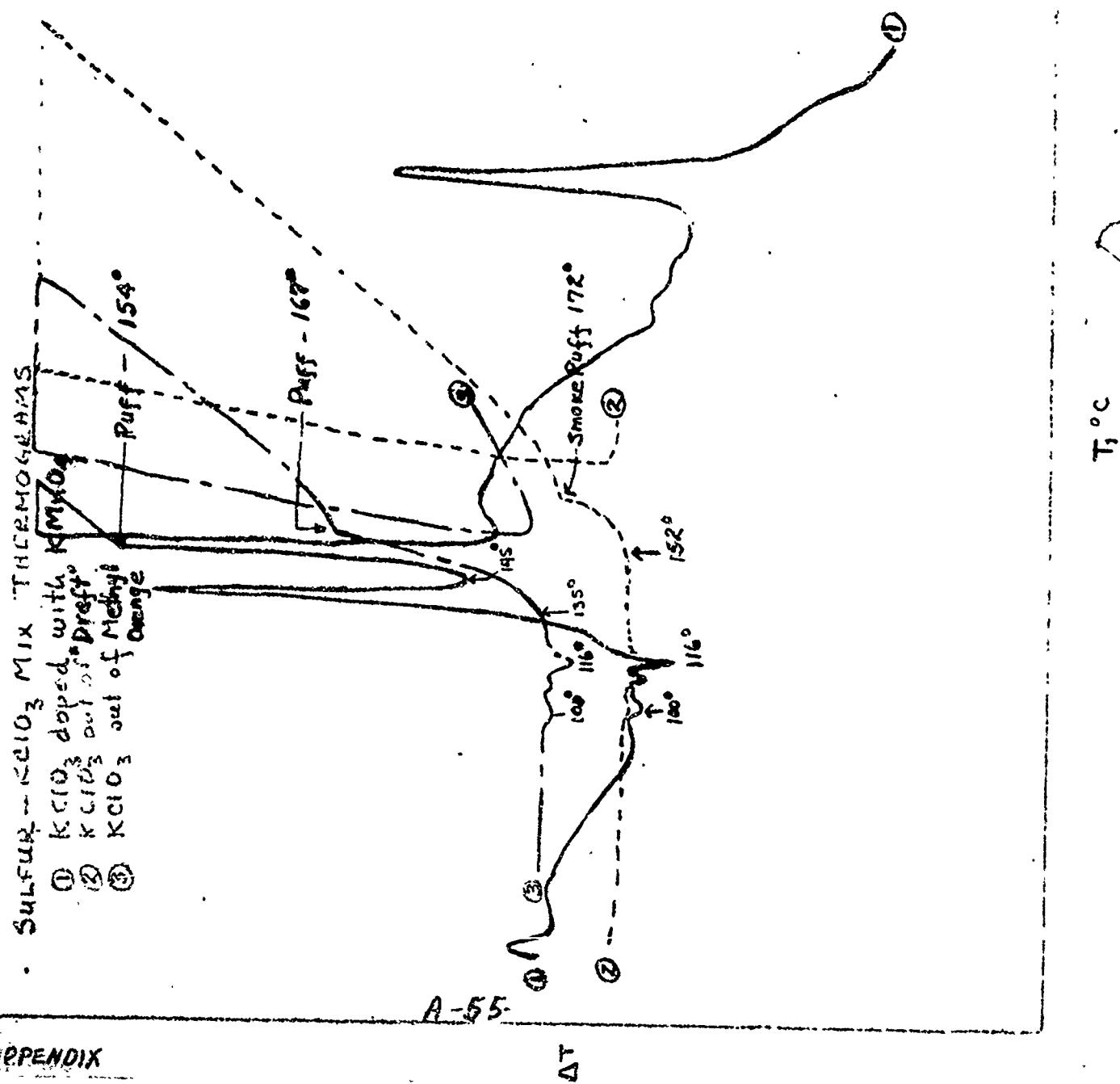


FIGURE 15



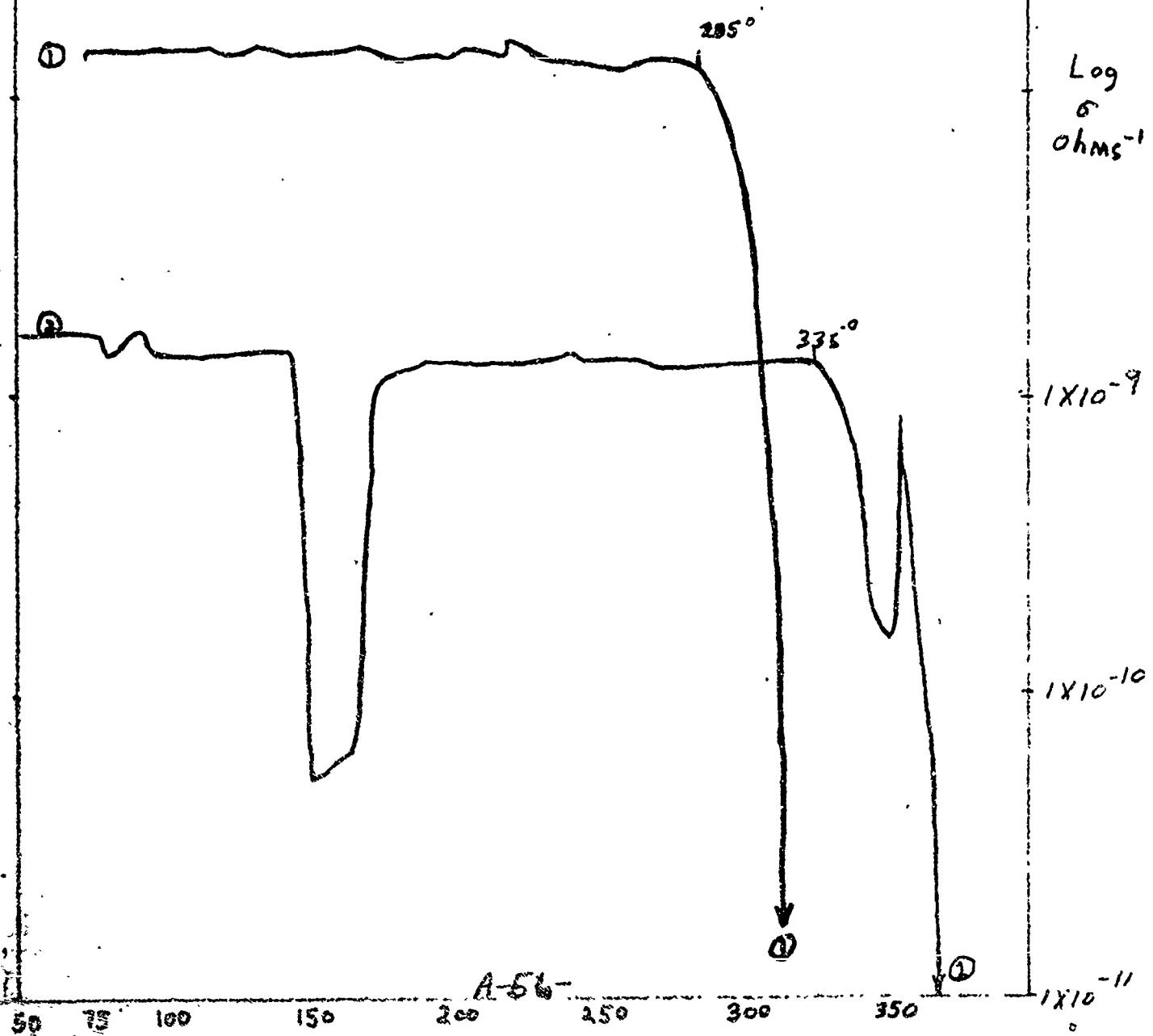
THERMOCONDUCTIMETRIC ANALYSIS

$\text{BaO}_2\text{-Fe}$ Two Runs on
78-22 two different sized pellets.

FIGURE 16

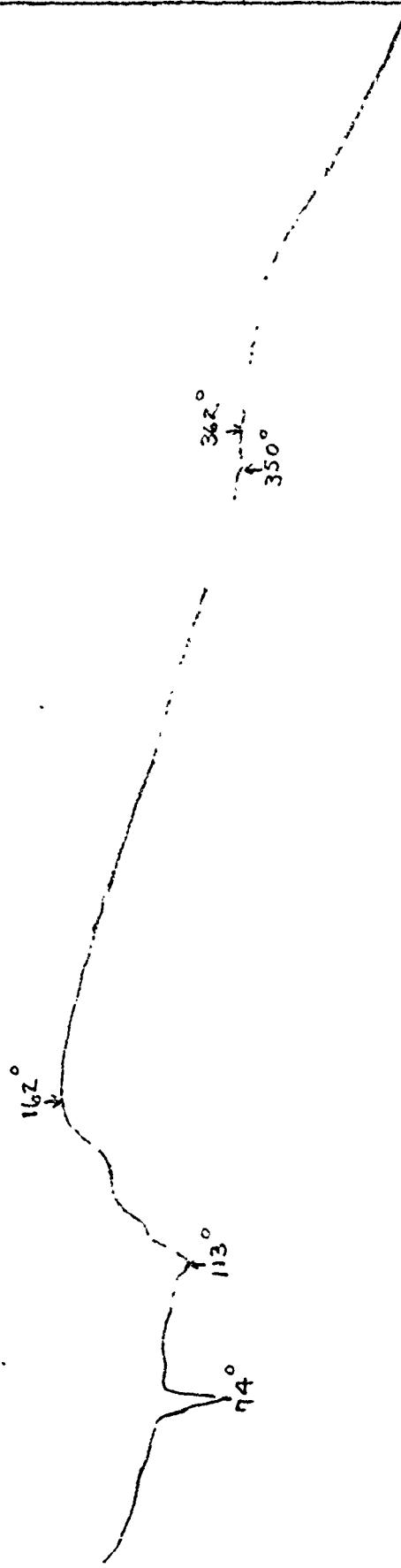
 1×10^{-6} 1×10^{-7}

Log
 σ
 ohms^{-1}

 1×10^{-9} 1×10^{-10} 1×10^{-11} 

BaO_2 - Fe
18 - 22

FIGURE 17



A-57-

APPENDIX

Thermoelectric Conductometric Analysis

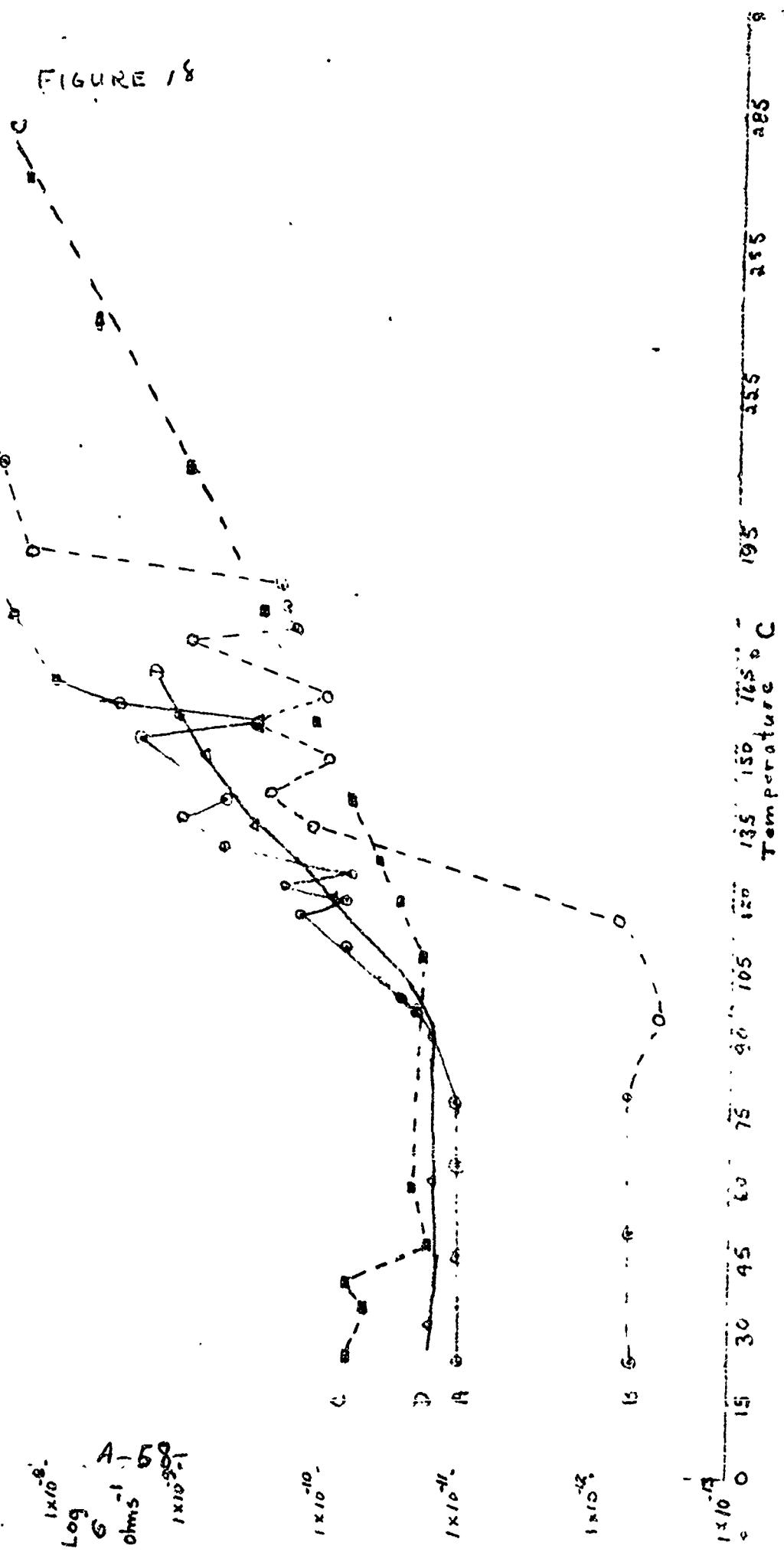
KClO₃ Pellets

uncorrected for pellet length and density

A) All the same but run one each day
 B } for 4 days
 C }
 D }

$\log \sigma$
 σ ohms⁻¹
 10^3

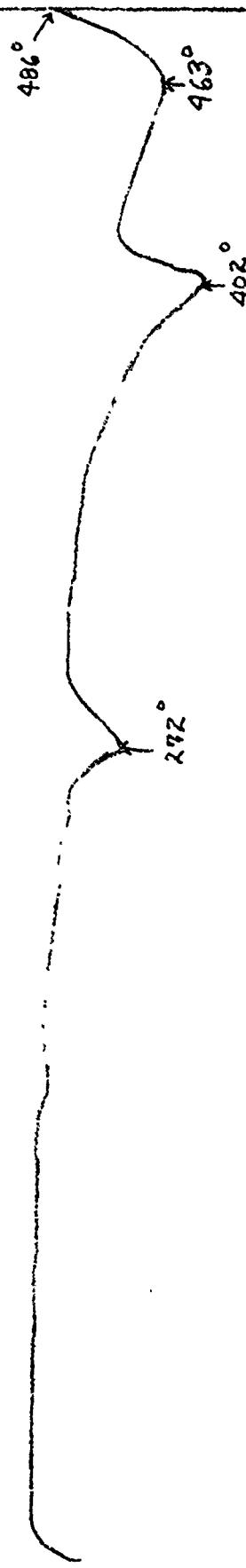
FIGURE 18



PbO - Si THERMOCOUPLE
80-20, 14 months old

Date - 6/8/65

Figure 19



T, °C (CHROMELE- ALUMEL)

A-59-

APPENDIX

ox3 ← ↑ → opu3

• THERMOCOCONDUCTIMETRIC ANALYSIS
• PbO-Si₂ Pellets

FIGURE 20

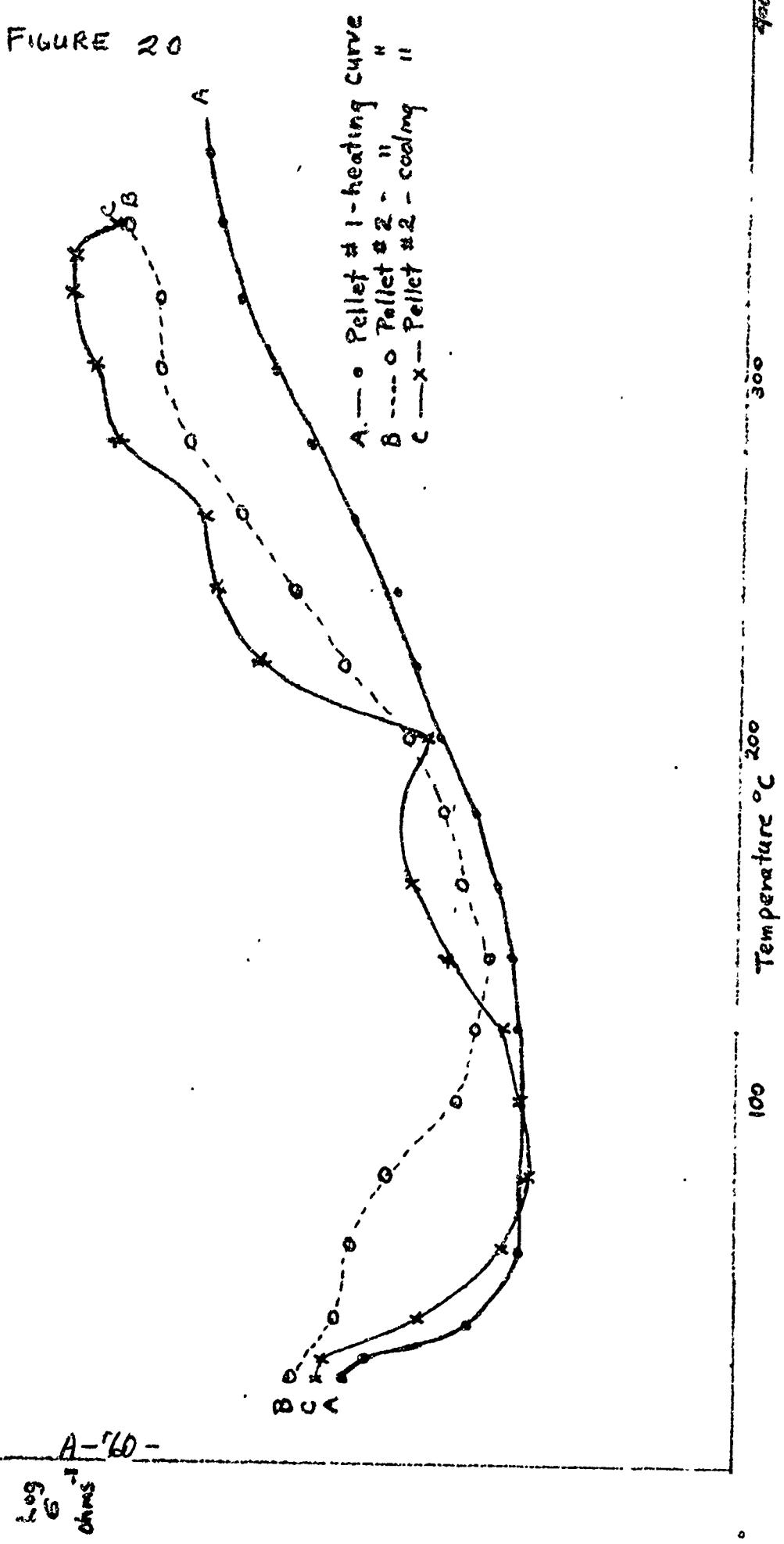
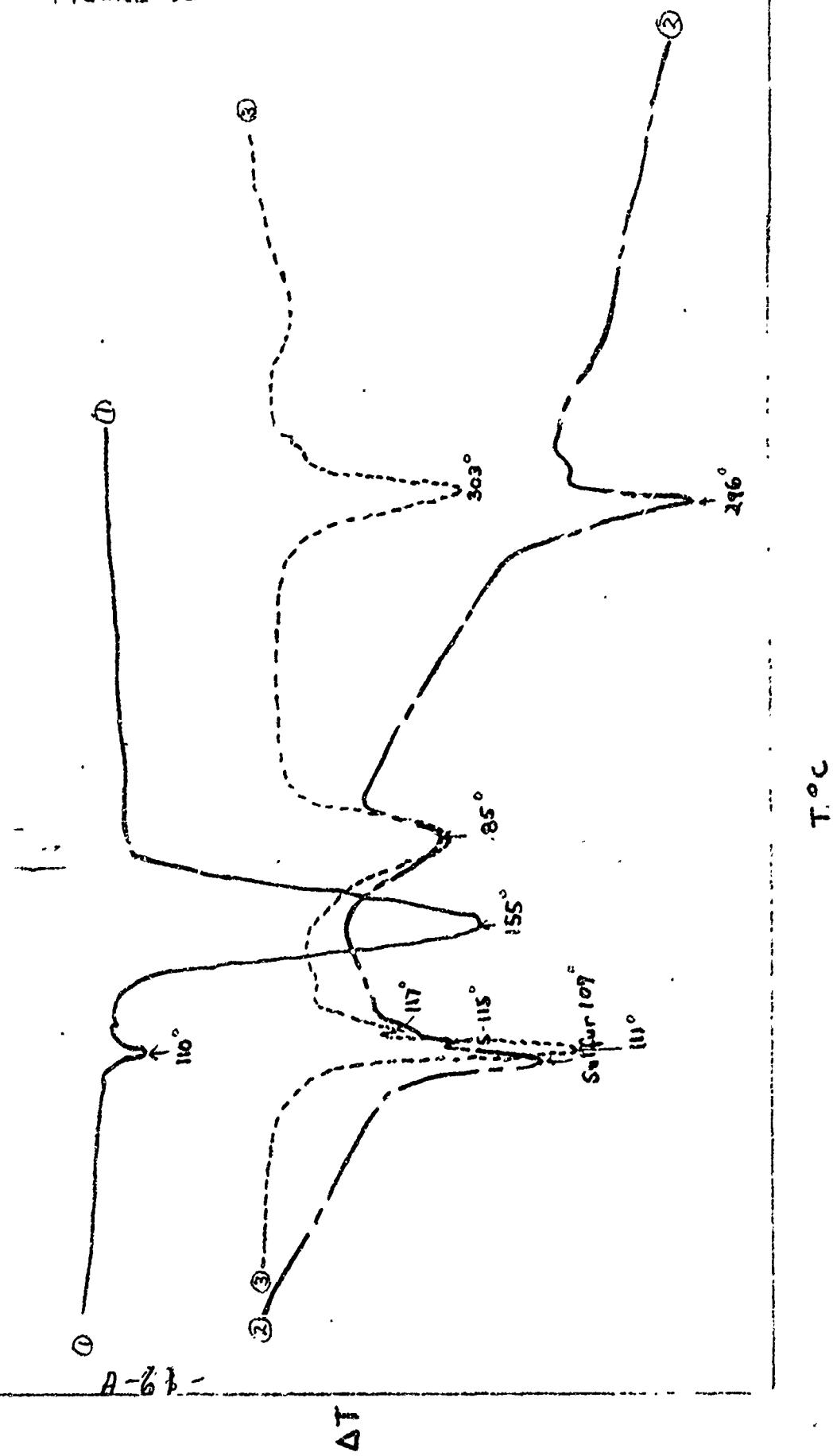


FIGURE 21

NaHCO_3 , THERMOGRAMS

- ① USP POWDER - CRDL
- ② Army Spec + Sulfur
- ③ " " + "



APPENDIX

Thermocolorimetric Analysis

PbO Pellets

uncorrected for pellet length and density

APPENDIX

FIGURE 22

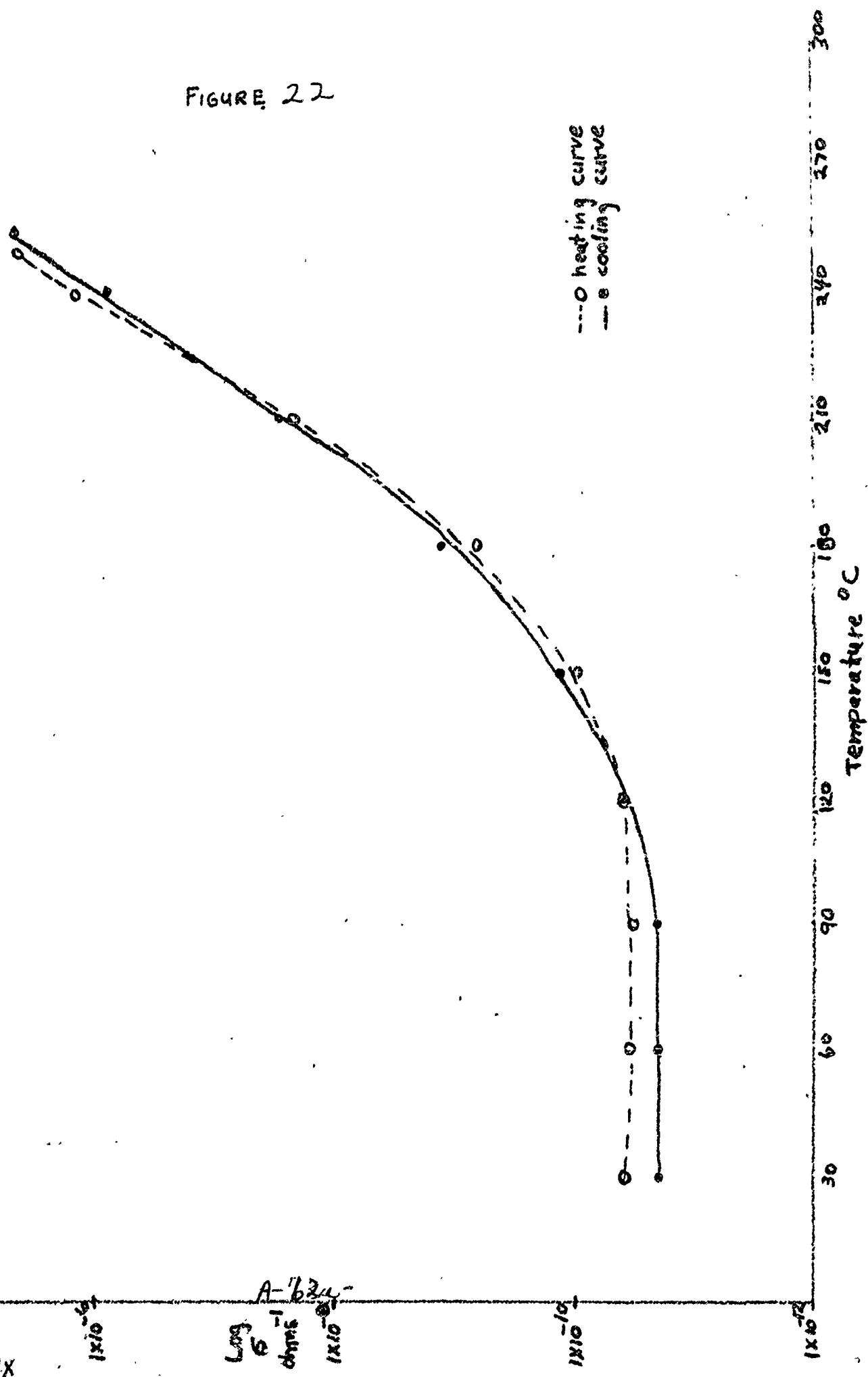
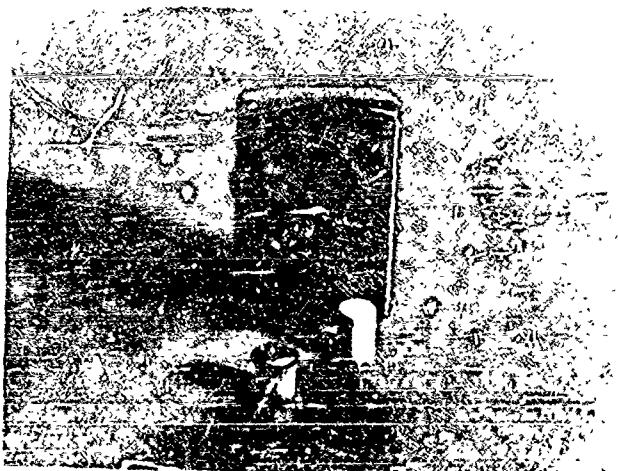
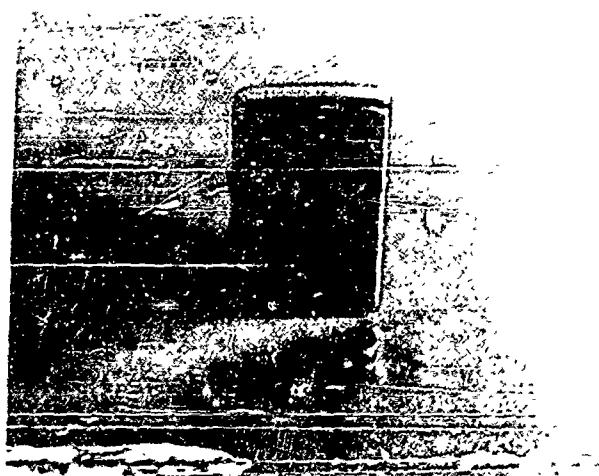


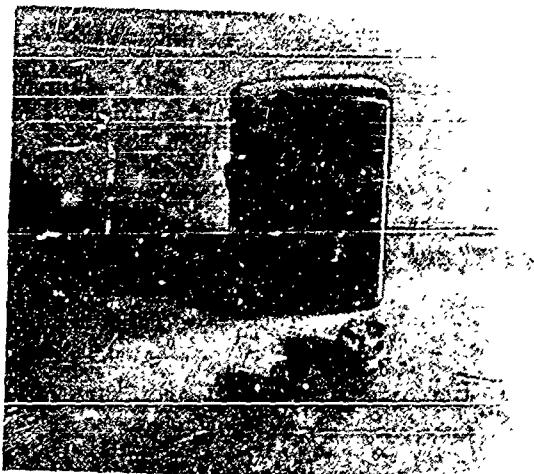
FIG. 23



Potassium chlorate —
before and after conductivity
measurements to 315°C.



Iron - barium peroxide
before and after conductivity
measurements to 368°C.



Iron - potassium dichromate
before and after measure-
ments to 400°C.

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13. ABSTRACT As a result of differential thermal analysis, thermoconductimetric analysis and burning rate studies on potassium chlorate, sulfur, sodium bicarbonate and their mix- tures the effect of phase transitions on reactivity has been evaluated. This evaluation has led to a postulated mechanism for the sulfur-potassium chlorate reaction in which the thermal decomposition of pure potassium chlorate is considered unimportant. A relatively new tool (thermocconductimetric analysis) for measuring effect of temperature on solid state reactivity has been developed and applied with satisfactory results. It has been determined that the reactivity of solid potassium chlorate can be en- hanced greatly by doping the crystalline material changing crystal habit and coating the crystals. A supersensitive potassium chlorate (doped with copper chlorate was prepared which when mixed with sulfur detonated on standing at room temperature.		

KEY WORDS

Differential thermal analysis
Thermoconductimetric Analysis
Potassium chlorate
Sulfur
Thermal decomposition
Hedvall Effect
Solid state
Hot Spot Theory
Doping
Copper chlorate
Detonation
Ignition temperature
DTA
TCA